# METHYLMERCURY CONCENTRATIONS IN FISH FROM TIDAL WATERS OF THE CHESAPEAKE BAY

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A message to Maryland's citizens

The Maryland Department of Natural Resources (DNR) seeks to preserve, protect and enhance the living resources of the state. Working in partnership with the citizens of Maryland, this worthwhile goal will become a reality. This publication provides information that will increase your understanding of how DNR strives to reach that goal through its many diverse programs.

C. Ronald Franks
Secretary

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**Methylmercury Concentrations in Fish from Tidal Waters of the**

**Chesapeake Bay**

# Final Report

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CBL          Chesapeake Biological Laboratory, University of Maryland Center for Environmental Science

DO           Dissolved Oxygen

DOC        Dissolved Organic Carbon

Hg           Mercury

HgT         Total Mercury

MeHg       Methylmercury

MD DNR    Maryland Department of Natural Resources

MDE         Maryland Department of the Environment

PON         Particulate Nitrogen

SRM         Standard Reference Material

TSS          Total Suspended Solids

USEPA      United States Environmental Protection Agency

USFDA      United States Food and Drug Administration

POC         Particulate Carbon

WHO        World Health Organization

STB         Striped Bass

WHP        White Perch

LMB         Largemouth Bass

## EXECUTIVE SUMMARY

Concerns for human and ecosystem health have provided a basis for the increased attention on studying mercury (Hg) in the environment. Public health warnings and guidelines for consumption of fish with elevated levels of methylmercury (MeHg) have been issued by many organizations. A MeHg-based fish consumption advisory was issued by Maryland Department of the Environment (MDE) in late 2001 based on measurements of MeHg in largemouth bass from MD reservoirs (Mason and Sveinsdottir, 2003) and other fish sampled by Maryland Department of Environment (MDE). Atmospheric deposition of Hg in Maryland is higher than in most other regions of the USA (Mason et al., 2000) and thus, based on the assumed higher Hg input, there is an expectation that fish should have higher Hg levels. Previous Maryland Department of Natural Resources (MD DNR)-funded studies in reservoirs demonstrated this to be the case. However, this did not appear to be the case for the Chesapeake Bay, based on historic data (Gilmour, 1999; Gilmour and Riedel, 2000). The current study was designed to examine in more detail the concentration of MeHg in fish that inhabit the tidal portion of the Chesapeake Bay, specifically striped bass (STB), white perch (WHP) and largemouth bass (LMB), all recreationally important species. Furthermore, the comparison of data for LMB between the reservoirs and this study allowed the examination of the potential differences in Hg concentration between reservoir and estuarine fish of the same species.

The sources of Hg to aquatic systems are both natural and anthropogenic. However, the most important source of MeHg is not external but is *in situ* production within aquatic systems by sulfate-reducing bacteria (Benoit et al., 2003). The concentration of MeHg varies among ecosystems and is not directly related to the amount of atmospheric Hg deposition, as the ability of the ecosystem to convert Hg to MeHg, and for the MeHg to bioaccumulate, depends on many physicochemical variables. Given the above, this project was formulated to determine the concentrations of total Hg and MeHg in muscle tissue of LMB, STB and WHP, representative of top predator and/or important recreationally-fished species in the mainstem Chesapeake Bay, and how these concentrations vary with fish size. In addition, the study was designed to probe variability in fish total Hg and MeHg concentration and investigate potential influential factors controlling MeHg in fish. The results indicate that, while fish concentration increased with size, there was substantial variability in the rate of increase between species and, for resident fish, between locations. Many chemical factors, such as water Hg and MeHg concentration, pH, dissolved organic carbon, as well as physical factors influence MeHg levels in fish. The results of this initial limited study indicate that there are a number of variables that correlate with fish MeHg concentration and that there is variability among species with similar diets. In addition, this study shows that the assumption, which is often made, that essentially all the Hg in fish muscle tissue is MeHg is not valid for some of the species identified here. Much more study of the form of Hg in estuarine and coastal fish needs to be done to examine this issue further. In addition, while the limited examination of the effect of migration on tissue MeHg levels did not provide a conclusive answer, when combined with other literature, it appears clear that the life history of the fish is an important determinant of its MeHg levels. The levels of MeHg in estuarine fish are lower than in reservoir fish for similar species, although it is difficult to directly

quantify this as only LMB are typical residents of both ecosystems. However, it appears that, for comparably sized fish, reservoir LMB can have up to 10 times the concentration of MeHg than LMB in the tidal fresh portion of the Bay. More studies are needed to further investigate the conclusions of this study, and to investigate further the factors controlling the concentration of MeHg in estuarine fish of the Chesapeake Bay and other Maryland waters.

**CHAPTER 1: INTRODUCTION**

*1.1 Background*

In recent years, concerns for human and ecosystem health have provided a basis for increased attention on studying mercury (Hg) in the environment. Mercury occurs naturally in a variety of inorganic and organic compounds, not only in solid or dissolved states, but also in liquid and gas phases (Meili, 1994). While Hg is mostly emitted to the atmosphere in the form of inorganic Hg – elemental ($Hg^0$) and ionic $Hg^{II}$, the majority of the Hg in fish, and the cause for the health concerns, is methylmercury (MeHg), a more toxic and bioaccumulative form of Hg. MeHg has a large capacity for biomagnification in food webs either through uptake from water or diet (Rodgers and Beamish, 1983).

Atmospheric deposition of Hg is often the dominant source of Hg to aquatic systems (Hakanson et al., 1988; Rolfhus and Fitzgerald, 1995) and the sources of Hg to the atmosphere are both natural and anthropogenic (Mason et al., 1994; Mason and Sheu, 2002). Mercury is emitted to the atmosphere from natural sources, such as from volcanic eruptions, forest fires, biogenic emissions, degassing from water surfaces and wind entrainment of dust particles (Rasmussen, 1994). Anthropogenic emissions of Hg are mostly from coal combustion, municipal and medial waste incineration, smelting and other industrial activities (Lindquist et al., 1991; Mason and Sheu, 2002). Anthropogenic inputs exceed the inputs from the natural sources by at least three-fold (Mason et al., 1994; Mason and Sheu, 2002) with higher levels in developed locations and around point sources, as we have demonstrated for Maryland (MD) (Mason et al., 1997; Mason et al., 2000). Population growth and urbanization have contributed to significantly elevated levels of Hg in sediment, water, and the atmosphere in MD coastal waters (Mason et al., 1999; Mason and Lawrence, 1999). However, the impact of elevated levels on the concentrations of MeHg in fish in the mainstem Chesapeake Bay has not been adequately examined. The current project was designed to address this issue.

Sources of MeHg to aquatic systems are from precipitation, typically a minor source, from in-lake methylation and from runoff from wetlands (Watras et al., 1995; Rudd, 1995). It has been estimated that sediment is an important sink for both Hg and MeHg in the aquatic environment, as shown for the Chesapeake Bay (Mason et al., 1999; Mason and Lawrence, 1999). After atmospheric deposition and runoff from surrounding catchments, Hg can be converted to MeHg via *in situ* production by natural bacteria in anoxic sediments and soils (Gilmour et al., 1992; Benoit et al., 2003). The amount of MeHg in aquatic regions varies among ecosystems (Benoit et al., 2003), as does the input from atmospheric Hg deposition. Therefore, MeHg bioaccumulation in fish not only depends on how much Hg enters the ecosystem, but also on the ability of an ecosystem to convert that Hg to MeHg (Heyes and Gilmour, 1999; Benoit et al., 2003). For example, methylation of Hg has been found to be enhanced in wetlands but may be produced in other anoxic regions as well. Increased runoff from highly urbanized areas, as the result of impervious surfaces in and around the watershed, may contribute to higher than normal inputs of Hg and MeHg into aquatic systems (Mason and Sullivan, 1998). It may not, however, result in higher levels of MeHg in fish as expected. Similarly, highly contaminated environments, such as Baltimore Harbor, may not have as elevated MeHg in fish because of non-linearities between total Hg input and MeHg formation and bioaccumulation (Benoit et al., 2003), and between MeHg concentration in water and

sediment and MeHg in biota, especially benthic organisms (Lawrence et al., 1999; Lawrence and Mason, 2001; Mason and Lawrence, 1999).

Once MeHg has been taken up by organisms low in the food chain (such as phytoplankton and zooplankton and benthic invertebrates), it is efficiently accumulated and transferred to organisms higher in the food chain (Mason, 2001). Accumulation of MeHg by fish is of concern since consumption of MeHg-contaminated fish is the major route for transfer of mercury from the aquatic environment to fish-eating birds and mammals, including humans (Rodgers, 1994). Exposure to high levels of MeHg has been found to cause neurological damage, as well as fatalities, among adults (Fitzgerald and Clarkson, 1991). Prenatal life and small children are even more susceptible to brain damage due to their enhanced sensitivity to the neurotoxin (Weiss et al., 1999).

The burden of MeHg in fish is suspected to depend on many physicochemical variables of the watershed environment and water-column. Water chemistry is likely to be an important factor controlling bioaccumulation rate and the concentration of MeHg in fish at any one time. Hg and MeHg concentrations, water temperature, dissolved oxygen (DO), dissolved organic carbon (DOC), pH, total suspended solids (TSS), particulate organic carbon (POC), particulate organic nitrogen (PON), and sulfate concentrations are among the chemical variables that influence both methylation of Hg and the uptake and accumulation of MeHg by fish from sediment and the water-column (Benoit et al., 2003). DOC and pH are probably the most important chemical variables influencing MeHg accumulation by fish (Mason, 2001), although many other chemical parameters that influence Hg speciation in the water column and ultimately affect the bioavailability of MeHg to biota, could also be contributing factors. Physical parameters of the watershed may influence the amount of MeHg in the aquatic environment but these are unlikely to have a direct impact on bioaccumulation of MeHg in aquatic organisms. In the study of Maryland reservoirs, total water column MeHg concentration correlated most strongly with LMB tissue levels. Other important variables were chloride and sulfate concentration, lake area/volume, and lake depth (Mason and Sveinsdottir, 2003). In a study of fish in MD streams, Mason (2000) concluded that important parameters were DOC, ANC, pH, and MeHg concentrations.

Public health warnings and guidelines for consumption of fish with elevated levels of MeHg have been issued by the World Health Organization (WHO, 1990), in parts of Scandinavia and Canada, by the U.S. Food and Drug Administration (USFDA, 2002), the US Environmental Protection Agency (USEPA, 1987) and numerous other agencies and governments. Until recently, USFDA regulations stated that fish containing less than 1ppm MeHg was safe for human consumption (USFDA, 2002) but this regulation is being re-examined by US regulatory organizations. In March 2001, USEPA and USFDA posted a consumer advisory about the risk of mercury in fish, advising pregnant women, and women of childbearing age who may become pregnant, and young children not to eat large fish that accumulate the highest levels of MeHg (USFDA, 2002). In the USA, there is more fish consumption advisories posted for Hg than for any other contaminant. However, until recently there was no Hg based fish consumption advisories posted in MD even though atmospheric deposition of Hg is higher than in most other regions of the USA (Mason et al., 1997; Mason et al, 2000). In December 2001, MD released an advisory based on the preliminary results from our previously funded MD DNR study (Mason and Sveinsdottir, 2003), and from the results of MDE and others

(MDE, 2004), that showed that Hg concentrations in large piscivorous fish from the state's freshwater lakes exceeded a common advisory level of 0.3 mg MeHg/kg wet weight, and in some cases exceeded the USFDA action level of 1 mg MeHg/kg in fish tissue (Gilmour, 1999; Sveinsdottir, 2002; Gilmour and Riedel, 2000; Mason and Sveinsdottir, 2003). However, preliminary data on tissue concentrations for Chesapeake Bay fish indicated lower levels than found in the reservoirs for fish occupying similar trophic levels (Gilmour, 1999). However, data was insufficient to clearly demonstrate this. One potential reason for lower levels is that some fish such as striped bass (STB) are migratory and therefore may not reside in one location, and may indeed spend part of their life in coastal and open ocean waters where Hg and MeHg concentrations are lower (Mason et al., 2001).

In summary, Hg contamination in freshwater fish stocks has been recognized as a problem in Europe and North America for over three decades, because consumption of fish is the largest source of MMHg in the human diet (WHO, 1990) and that of fish-eating wildlife. Sources of MeHg to aquatic system are from precipitation, in-lake methylation and runoff from wetlands (Rudd, 1995) but, in most instances, *in-situ* methylation is the dominant source (Benoit et al., 2003). Studies of Hg in MD aquatic systems have been somewhat limited. Fish in MD reservoirs have elevated Hg concentrations but other factors besides the amount of Hg deposition also influence the levels of MeHg in fish (Mason and Sveinsdottir, 2003) so these results cannot be extrapolated directly to the Chesapeake Bay. For the Chesapeake Bay, Mason et al. (1999) estimated that more than 60% of the MeHg in the Chesapeake Bay system is derived from *in situ* methylation. The current study was designed to ascertain, in more detail, the levels of MeHg in recreationally important fish of the Chesapeake Bay and the potential factors influencing the accumulations of MeHg in these fish.

*1.2 Objectives*

In light of the discussion above, the project was formulated under the following objectives:

1) Determine the concentrations of total Hg and MeHg in muscle tissue of top predator fish in the tidal portion of the Chesapeake Bay, and examine how these concentrations vary with fish size;

2) Determine the relationships between location in the Bay and fish concentration, and to ascertain, through the use of otolith analysis, the importance of migration on influencing fish MeHg concentration for striped bass; and

3) Determine the concentration of MeHg in representative food organisms and in the water and sediment to ascertain the principal factors influencing bioaccumulation.

Overall, the study was designed to provide the necessary information for evaluation of the extent of the problem of MeHg in fish in the Chesapeake Bay. Given the somewhat limited nature of this study, due to the limitation in funds available, the information collected is not sufficient for a comprehensive and exhaustive analysis. However, the data provides a suitable basis for managers to set regulations, if necessary. In addition, the study will provide further information to allow the continual refinement of our understanding of the factors regulating Hg and MeHg fate and transport in the environment, and of the propensity for fish concentrations to either increase, decrease or remain the same in the future, and how directly changes in Hg inputs may affect this.

This study thus forms both a starting point and a building block for future endeavors to understand the factors controlling MeHg concentration in Maryland fish in the Chesapeake Bay and its tributaries.

# CHAPTER 2: MATERIAL AND METHODS

## 2.1 Fish Collection and Analysis

      2.1.1   Fish Collection.  Fish were collected by various methods and at various locations in the Chesapeake Bay and its tributaries. In Fall 2002, striped bass (*Morone saxatilis*) were collected by MD DNR personnel at two locations in the Chesapeake Bay (Fig. 2.1): 1) off Point Lookout, which is at the mouth of the Potomac River, and is therefore representative of the mid to lower portion of the Chesapeake Bay, and 2) off Deale, which is representative of the mid-Bay region. These fish were collected using pound nets and were generally of smaller size, between 1-2 kg. Also in Fall 2002, largemouth bass (*Micropterus salmoides*) were collected from the tidal reaches of the Chesapeake Bay and its tributaries by MD DNR personnel by electroshocking. This technique does not sample the larger fish typically, and the fish obtained were less than 1 kg. Locations included the upper Bay and near the mouth of the Susquehanna River (Fig. 2.1).
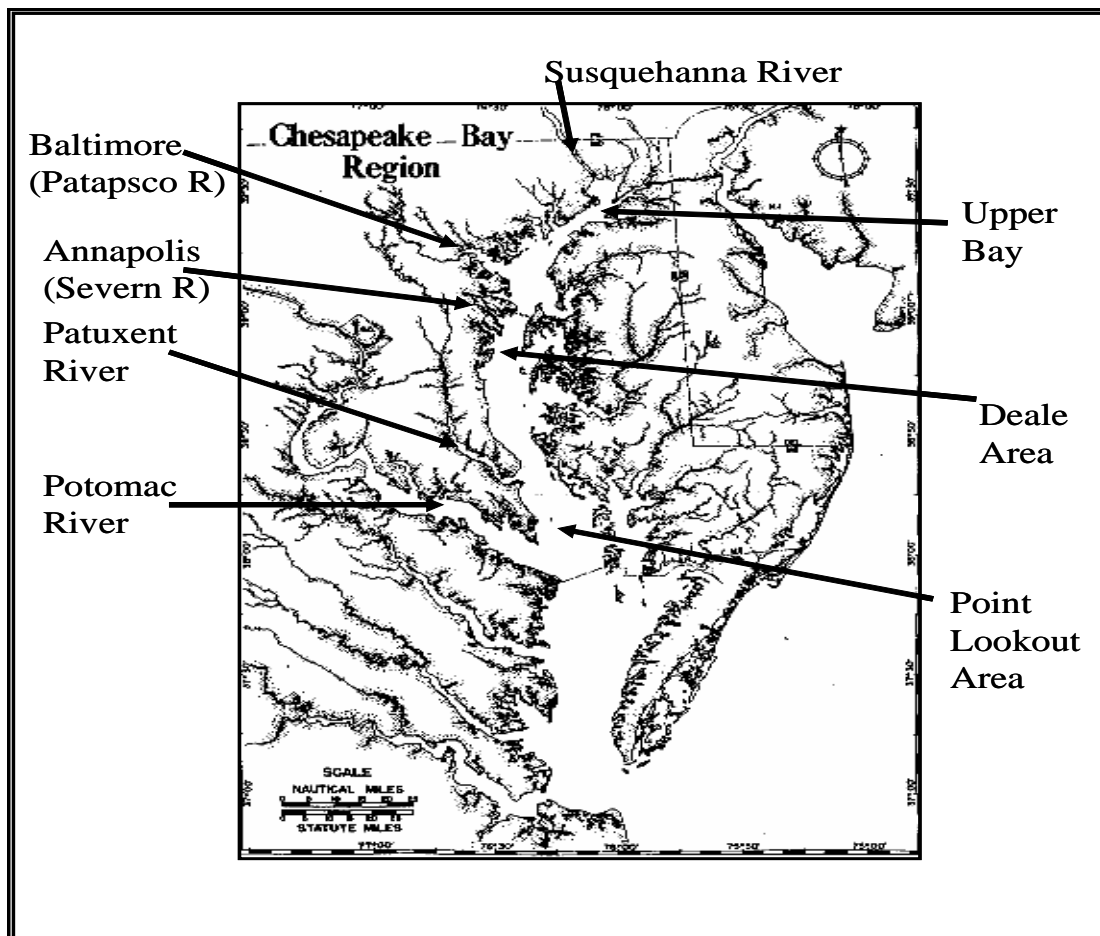


Figure 2.1: Map of the Chesapeake Bay showing the sampling site locations.

In spring 2003, white perch (*Morone americana*) were collected from the Choptank River, which flows into the mainstem mid-Bay, and the Severn River, near Annapolis. MD DNR personnel collected all these samples using nets. Other white perch (WHP) were obtained from MDE, collected as part of their routine fish monitoring program (MDE, 2004). These fish were from the Patapsco River, rivers on the Upper and Lower Eastern Shore, from the South River near Annapolis, and from the Potomac and Patuxent River (Fig. 2.1). The large mouth bass samples (LMB) came from the upper reaches of the Chesapeake Bay. In addition, striped bass (STB) samples were collected in Spring 2003 and Summer 2004 by individual anglers and samples were provided to CBL for analysis. These fish were caught from the mid to upper Bay (mouth of the Potomac to the mouth of the Susquehanna). Fish were caught during the spring migration in 2003 in an effort to obtain samples from large fish and were caught using typical angling techniques (rod+reel). To further enhance the dataset, additional samples were provided by the same fisherman of fish caught during the summer of 2004. It was not possible to ascertain the exact location of capture in each case but as STB move widely throughout the Bay and also migrate offshore, the location of capture is not necessarily representative of the location where the fish typically resides.

Both STB and WHP are estuarine species while LMB are a freshwater species. STB are found in shallow coastal waters and migrate in and out of the estuaries, especially as they get older (Mansueti, 1961). To determine the extent to which the STB were resident species, otoliths were collected for analysis from fish, where possible, and were analyzed for their strontium (Sr) to calcium (Ca) ratio. This ratio gives an indication of the life history of the fish. While it is possible to analyze the otoliths in detail to obtain yearly information on migration patterns (e.g., Secor et al, 2001), this was not possible under the scope of this project because of budget limitations. Ocean Sr:Ca molar ratios in water are between 8.5-9 mmol mol$^{-1}$ and freshwater values tend to be much less (typically <5), although they can be highly variable (Kraus and Secor, 2004). Analysis of the whole otolith provides some indication of the migratory behavior of the fish throughout its lifetime.

In the field, all fish were handled by gloved personnel, and after rinsing and measurement, each fish was bagged in a plastic Ziploc bag. The fish were kept cold (on ice), with each bagged fish wrapped in aluminum foil and then bagged in a second Ziploc bag. Fish were kept on ice and shipped overnight to the Chesapeake Biological Laboratory (CBL), or were picked up in the field by CBL personnel. At CBL, the weight and length of each fish was measured if this had not already been done. Once in the laboratory, fish were filleted and muscle tissue from both sides of each individual fish (representing the portion of fish normally consumed by humans) was removed and homogenized in blender in a non-contaminating environment and then stored frozen in a Ziploc bag until further analysis. All sampling equipment, such as stainless steel knives and food processors, were acid cleaned prior to use and in between fish. In addition, otoliths were removed and washed in distilled water and stored for analysis, when possible.

2.1.2 Methylmercury Analysis. For MeHg analysis of fish, approximately 1 g of sub-sampled homogenized axial muscle was placed in a Teflon vial. Samples were digested in an alkaline digest (Bloom, 1989) prior to derivitization with sodium tetraethylborate to convert nonvolatile MeHg to gaseous MeHg (Bloom, 1989). The

volatile adduct was then purged from solution and collected onto a graphitic carbon trap. The MeHg was then thermally desorbed from the trap and analyzed by isothermal gas chromatography separation with cold vapor atomic fluorescence spectroscopy (CVAFS). For fish, all concentrations are reported on a wet weight basis.

The following QA/QC was performed. Laboratory blanks and duplicates were part of all analytical runs, as were matrix spikes and analysis of standard reference materials (Table 2.1). Blanks were typically a small fraction (<10%; <0.1 ng in the digestate) of the sample concentration (1-1000 ng in the digestate). Analytically, to ensure good results, blanks should be <20% of the sample value. However, the precision of the blank measurement defines the detection limit and thus analytically it is possible to quantify the concentration of a sample in which the blank value is a much larger fraction of the sample value, although this did not occur with these samples.

In a previous study, an analysis of the concentration of MeHg in one fish sample was done eleven times during a 17-month period (Mason and Sveinsdottir, 2003). Results from this analysis showed that MeHg concentrations in the fish sample remained stable over this period and concentration did not decrease with time (mean = $20.5 \pm 4.7$ ng/g wet weight, slope not significantly different from 0). Thus, storage time between collection and analysis does not influence measured concentration.

Table 2.1: Quality control parameters for analysis. The detection limit (DL), percentage relative standard deviation (%RSD) for laboratory and field duplicates, typical spike recoveries and field blanks are given for mercury (Hg) and methylmercury (MeHg).

| Metal | DL Water* | DL Fish | % RSD[#] | % Recovery of Matrix Spike | Field Blank* |
|-------|-----------|---------|----------|----------------------------|--------------|
| Hg | 0.1 | 0.05 | $10 \pm 5$ | 80-120 | <1 |
| MeHg | 0.01 | 0.015 | $10 \pm 5$ | 80-120 | <DL |

*Detection limit (DL) and blank values are given in ng/L and ng/g.
#Values given for fish analysis.

Analysis of standard reference materials (SRM) typically yielded a value within the certified variance. However, if the SRM was not within the range of the certified value, the sample was reanalyzed. If the value was still not within compliance, the values for that batch of samples were not considered to be reliable and all samples were reanalyzed. Spike recoveries were done for every batch of samples. This involves the addition of a known amount of standard to a sample prior to the digestion procedure and the comparison of the concentration in the spiked sample and the sample itself allows an estimation of the amount of the analyte in the sample that was recovered. The range in values of spike recoveries is given in Table 2.1.

2.1.3  Total Mercury Analysis.  For total Hg analysis of fish, 0.4g of homogenized tissue was added to a Teflon vial with a 70% sulfuric/30% nitric acid solution and digested overnight at $60^{o}C$ (Mason and Sveinsdottir, 2003).  Samples were diluted to 10 mls with distilled deionized water and then treated as described below (Section 2.2.2) for water samples from the bromination (BrCl addition) step.  The QA/QC performance

criteria are detailed in Table 2.1 and were done in a similar fashion as described for MeHg above in Section 2.1.2. The same SRM was used for total Hg as for MeHg.

*2.2. Sediment and Water Sample Collection and Analysis*

2.2.1 Sample Collection. Samples have been collected in the Chesapeake Bay during a number of different projects. Samples were either collected by wading from shore, or from bridges and other structures or from a plastic Zodiac boat by hand-dipping 2 L Teflon bottles off the bow of the boat. Deep water samples and samples taken from structures were either collected using an 8 L Teflon-lined Go-Flo bottle (e.g., Mason et al., 1995), or a peristaltic pump with precleaned Teflon tubing. Samples collected by Go-Flo were immediately decanted into 2 L Teflon bottles. River samples were either collected by hand directly into Teflon bottles or were collected using a peristaltic pump and Teflon tubing. For all collections, the person taking the samples wore poly-gloves. All sample bottles were Teflon and were acid-cleaned using our established protocols prior to use (e.g., Mason and Sullivan, 1997). The bottles were rinsed three times prior to filling and then filled, double-bagged, and transported in coolers on ice back to the laboratory for analysis. All total and methylmercury (MeHg) analyzes were performed at CBL. Laboratory replicates consisted of subsamples from the same bottle. Field replicates consisted of duplicate collections at the same sampling location into separate bottles. Field blanks consisted of bottles filled with Hg-free water that were transported to the field and opened onsite.

2.2.2 Water and Sediment Analysis. Samples were analyzed using standard techniques for Hg analysis at low levels (e.g., Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988; Mason and Fitzgerald, 1990; Mason et al., 1993; USEPA, 1998; 1995). Quantification was by CVAFS. For total Hg, samples were oxidized using 0.2 N bromine monochloride solution (BrCl) for at least 30 minutes to release Hg from particles and organic complexes, then pre-reduced using hydroxylamine hydrochloride (Bloom and Crecelius, 1983), prior to quantification by tin chloride reduction-CVAFS. This method, outlined in EPA Method 1631 (EPA, 1995), is based on methods developed by Bloom and Crecelius (1983) and others (e.g., Gill and Fitzgerald, 1985; Bloom and Fitzgerald, 1988). MeHg was measured using a distillation technique (Horvat et al., 1993) prior to ethylation with sodium tetraethylborate solution and analysis by gas chromatography with quantification using CVAFS (Bloom, 1989). The detection limit (DL) for total Hg in water was typically <0.1 ng/L. For total MeHg, the DL was around 0.01 ng/L (Table 2.1).

Samples of sediment were also collected throughout the Chesapeake Bay and its tributaries. For total Hg in sediments, approximately 1 g wet weight of sample was digested overnight at $60^{o}$C using a 70%/30% sulfuric acid/nitric acid mixture to ensure complete digestion of organic matter (Bloom and Crecelius, 1987). The acid digest was further oxidized by the addition of 2 mL of BrCl, followed by hydroxylamine pre-reduction and quantification by tin chloride reduction-CVAFS. MeHg was determined on a separate subsample using distillation techniques. The DL for sediment was similar to fish (Table 2.1). Concentrations in sediments are reported on a dry weight basis.

2.3 *Otolith Analysis*

Saggital otolith pairs were removed from the fish and rinsed in Milli-Q water before being placed into clean polypropylene containers. The otoliths were dried in a laminar flow hood for 48 hours then stored until analysis. Just prior to analysis, the otoliths were cleaned by immersing them in 3% $H_2O_2$ for 5 minutes and then in 1% $HNO_3$ for 5 minutes, and were then rinsing copiously with Milli-Q water (Secor et al., 2001). The otoliths were weighed before and after cleaning and loss due to cleaning averaged 0.01g/otolith. The otoliths were then placed into clean polyethylene 15 ml scintillation vials and 1 ml of concentrated $HNO_3$ was added. After 3 hours, 9 ml of Milli-Q water was added to each scintillation vial. The otoliths were analyzed, after proper dilution, for Sr and Ca by ICP-MS using an internal standard (45 Sc) for Ca only.

# CHAPTER 3: METHYLMERCURY CONCENTRATIONS AND TOTAL MERCURY IN FISH AND FACTORS INFLUENCING BIOACCUMULATION

## 3.1 A Brief Life History of the Fish Species Sampled

All the fish analyzed are typically thought to be predators as adults but all fish have a varied and mixed diet of fish and invertebrates. The dominant food is fish for LMB and STB, although their diets also include invertebrates and other prey (Murdy et al., 1997). In a study in the Chesapeake Bay, Walter and Austin (2003) found that 44% by weight of the diet of STB was menhaden. In the mesohaline waters, mehanden was 60-65% by weight of the diet for fish of 458-711 mm in spring; 55-60% by weight in the fall. Other fish made up the bulk of the remainder of the diet. Diets of STB in spring in freshwaters portions of the Bay reflected the resident prey. The larger fish (>711 mm) fed mostly on gizzard shad (89% by weight) while the smaller fish fed mostly on river herring (50% by weight) and white perch and gizzard shad (20-25% each). For all STB, there was a weak correlation between fish size and prey size (Walter and Austin, 2003). For WHP, their diet is mostly invertebrates throughout their lifetime (Secor, pers. comm.). WHP are predaceous carnivores whose diet is a function of age. Smaller fish feed on crustaceans and aquatic insects while larger fish prey on crabs, shrimp, and small fish. While young LMB feed on plankton, insects and small fishes, the larger individuals are opportunistic and feed on a variety of prey, including crustaceans (crayfish) and fish (Jenkins and Burkehead, 1993; Murdy et al., 1997).

All species are also important recreational sport fish, and this was one reason they were the target species for this study. The LMB analyzed ranged in size from 150 to 180 mm in length, and weighed from 500 to 800 grams. Thus, they did not represent the overall potential size range as LMB can reach 610 mm in length, especially in lakes. Most adults in the tidal fresh waters are, however, under 450 mm in length. Electrofishing surveys in the tributaries of the Chesapeake Bay (Cosden, DNR, pers. comm.) confirm this as 75% of the fish typically are <350 mm in length. Thus, the differences in terms of size between the estuarine fish collected in this study and reservoir fish collected previously (Mason and Sveinsdottir, 2003) reflect the differences in the sizes of the fish in the two environments as the reservoirs tend to have more optimal habitat for LMB (extensive shallow areas for feeding; Murdy et al., 1997).

WHP sampled ranged in size from 120 to 250 mm. These sampled fish do not represent the larger size range for this species which can attain 480 mm. These fish, as they were caught in spring, likely represent year O+ or 1+ fish (Secor, pers. comm.). The database for WHP was however supplemented by the analysis of fish collected by MDE. WHP are year-round residents of all the tributaries of the Chesapeake Bay although in the Upper Bay the population is more mixed as the salinity is low enough that the fish can migrate between sub-estuaries (Secor, pers. comm.). While they inhabit the shallower reaches in the spring and summer, they are found primarily in the deeper channels in winter. They usually inhabit waters of <18 ppt salinity but can also be found in full strength seawater.

The STB caught in the fall of 2002 were overall smaller than those caught in the spring where large fish were targeted as they enter the Bay from the ocean to spawn. Fish as large as 17 kg were caught (range 0.5-17 kg) so that a large size range could be analyzed to determine the extent to which fish Hg concentration increased with age, and

whether migration may have a mitigating impact on fish MeHg concentration. STB can be found in the Bay all year and they tolerate a wide range of salinities. They inhabit the deeper waters in the winter and the older fish migrate offshore in the summer, returning to the estuary in the spring to spawn, beginning in early March and continuing until the end of April. Spawning occurs primarily in the upper freshwater reaches of the tributaries to the Chesapeake Bay. The STB that leave the Bay can range widely and they are distributed along the Atlantic seaboard, from Massachusetts to Cape Hatteras, although they remain in relatively shallow water (Mansueti, 1961). Thus, the larger STB have a range of life histories.



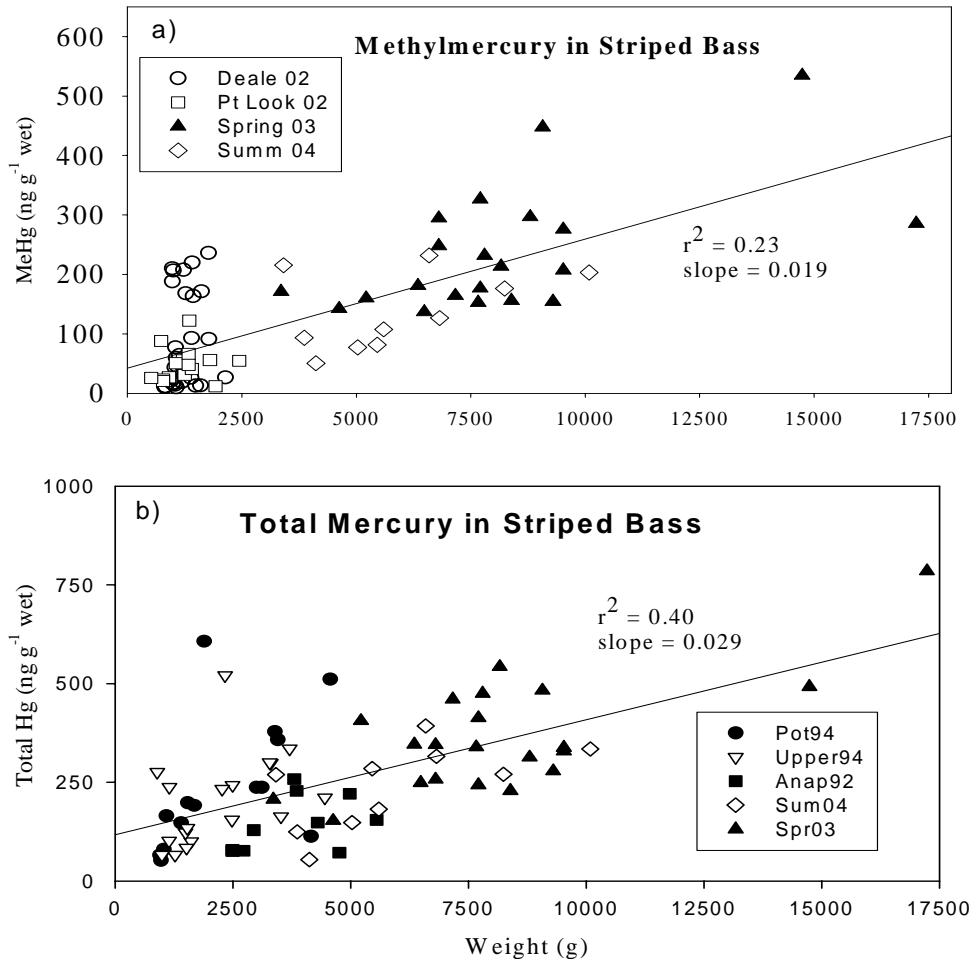Figure 3.1. Plot of the concentration of a) methylmercury (MeHg) and b) total mercury (Hg), both in ng g$^{-1}$ (ppb) wet weight, in striped bass from the Chesapeake Bay against fish weight. Data from this study and from Gilmour and Riedel (2000).

*3.2 Fish Mercury and Methylmercury Concentration*

    3.2.1 Striped Bass. The data for the size (length and weight) and MeHg concentration of the fish are gathered in Appendix 1. The data for MeHg for the STB collected from 2002-04 are plotted in Fig. 3.1a. There appears, overall, to be a significant increase in fish MeHg concentration with fish weight. However, overall, the concentrations are relatively low (< 300 ng $g^{-1}$ generally), especially for the larger fish compared to those of freshwater species of similar trophic status and size.

    The data collected for total Hg in 2003-04 is plotted in Fig. 31b and can be compared to concentrations of total Hg in STB from earlier studies in 1992 and 1994 by Gilmour (1999). These data are also plotted in Fig. 3.1b. The data for 1992 are from fish caught in the vicinity of Annapolis (Anap92). The 1994 data are from either the Potomac River (Pot94) or in the vicinity of Annapolis (Upper94). Overall, there appears to be small differences, given the scatter in the data, between the fish sampled ten years apart. However, there were some higher values, and more scatter, in the earlier data which consisted overall of smaller fish. The reason for this scatter is not known.

Table 3.1: Regression data for striped bass for either total mercury (Hg) concentration and weight, or methylmercury (MeHg) concentration and weight. NS = not significant.

| Sampling Location and Time | n | Slope (ng $g^{-1}$) $g^{-1}$ | Intercept (ng $g^{-1}$) | Regression Coeff., $r^2$ | Signif. |
|---|---|---|---|---|---|
| **Total Mercury** | | | | | |
| Spring 03 Mid/Upper | 21 | 0.033 | 94.1 | 0.50 | <0.01 |
| Summer 04 Mid/Upper | 10 | 0.031 | 52.8 | 0.37 | <0.05 |
| Potomac Fall 94 | 14 | 0.069 | 80.1 | 0.27 | 0.05 |
| Upper Bay Fall 94 | 18 | 0.047 | 99.3 | 0.19 | <0.1 |
| Annapolis Fall 92 | 10 | — | — | 0.19 | NS |
| All Fish | 73 | 0.031 | 117 | 0.40 | <0.01 |
| **Methylmercury** | | | | | |
| Spring 03 Mid/Upper | 21 | 0.019 | 74.5 | 0.34 | <0.01 |
| Summer 04 Mid/Upper | 10 | — | — | 0.20 | NS |
| Deale 02 | 32 | — | — | 0.051 | NS |
| Pt Lookout 02 | 15 | — | — | 0.012 | NS |
| All Fish | 77 | 0.022 | 42.4 | 0.54 | <0.01 |

    Correlations between fish weight and concentration were sought for the individual datasets and for the entire dataset for both MeHg and total Hg (Table 3.1). For the smaller datasets, the relationships were not significant. For MeHg, the overall relationship had a relatively flat slope (0.022 (ng $g^{-1}$) $g^{-1}$) which was similar to that of the spring 2003 fish. The correlations for the other groups of fish were not significant. For total Hg, the overall slope of the regression line was higher than that for MeHg suggesting that total Hg concentration is increasing relatively more rapidly than MeHg in these fish (Table 3-1). This is shown more clearly in Fig. 3.2 as the fraction of the total Hg as MeHg decreases with increasing total Hg concentration. It would be expected that larger STB would feed almost exclusively on smaller fish, as discussed above, and as a result should have the majority of the Hg in their muscle tissue as MeHg. Indeed, this is

mostly so for fish of <200 ng g$^{-1}$ wet weight total Hg. That the fraction as MeHg decreases with increasing total Hg, and, by correlation, with size, is unusual as it would rather be expected that the fraction as MeHg would increase, if anything, with increasing size as this has been shown for many species of fish. There are a number of potential reasons for this trend which will be discussed in more detail below.
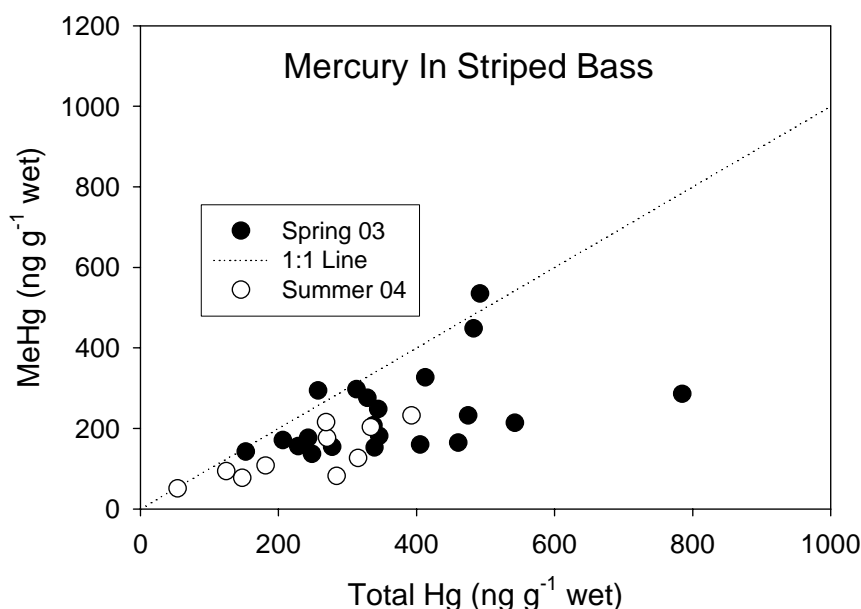


Figure 3.2: Relationship between total mercury (Hg) and methylmercury (MeHg) for striped bass caught in the Chesapeake Bay in 2003 and 2004.

The slopes of the relationships for the various groups of fish for total Hg and weight are all very similar (Table 3.1). The greatest slopes are for the 1994 Upper Bay and Potomac River fish. The relationship for the 1992 data was not significant. The combined slopes for the two 1994 datasets was also significant ($r^2$ = 0.23; slope = 0.058 (ng g$^{-1}$) g$^{-1}$) and substantially higher than that for the 2003-04 datasets ($r^2$ = 0.55; slope = 0.036 (ng g$^{-1}$) g$^{-1}$). The differences in the correlation slope suggest that STB were accumulating more Hg ten years ago than at present. There are little actual data for Hg inputs over this time period that may be used to corroborate or refute this inference. However, such a change would be consistent with regulation of atmospheric Hg sources in MD and elsewhere and in likely decreased inputs from point sources to the Bay.

The Maryland fish advisory concentration, based on an average assumed consumption of fish, is approximately 300 ng g$^{-1}$ wet weight (MDE, 2004) and thus most of the STB are below this action level. If this level is a valid measure, then consumption of most STB – all except the largest fish (>10 kg) – would not pose a significant health risk to pregnant woman and to woman of child bearing age and to children unless they were consumed in amounts, on a continuous weekly basis, above the average assumed consumption value (8 oz per week for adults, 3 oz per week for children) which is used in defining the advisory level.

3.2.2 Largemouth Bass. The range in fish weight for the LMB was relatively small and thus it is harder to make definitive statements about the relationship between weight and concentration. The MeHg concentrations found were very low (Fig. 3.3). Indeed, in comparison to the fish concentration data for largemouth bass from Maryland reservoirs there is an obvious and substantial difference in concentration for fish of similar weight (Table 3.2). However, there was also a substantial variability between reservoirs in this relationship (Mason and Sveinsdottir, 2003).

### MethylHg in Large Mouth Bass

Reservoir: $r^2$ = 0.29; slope = 0.23; p<0.01
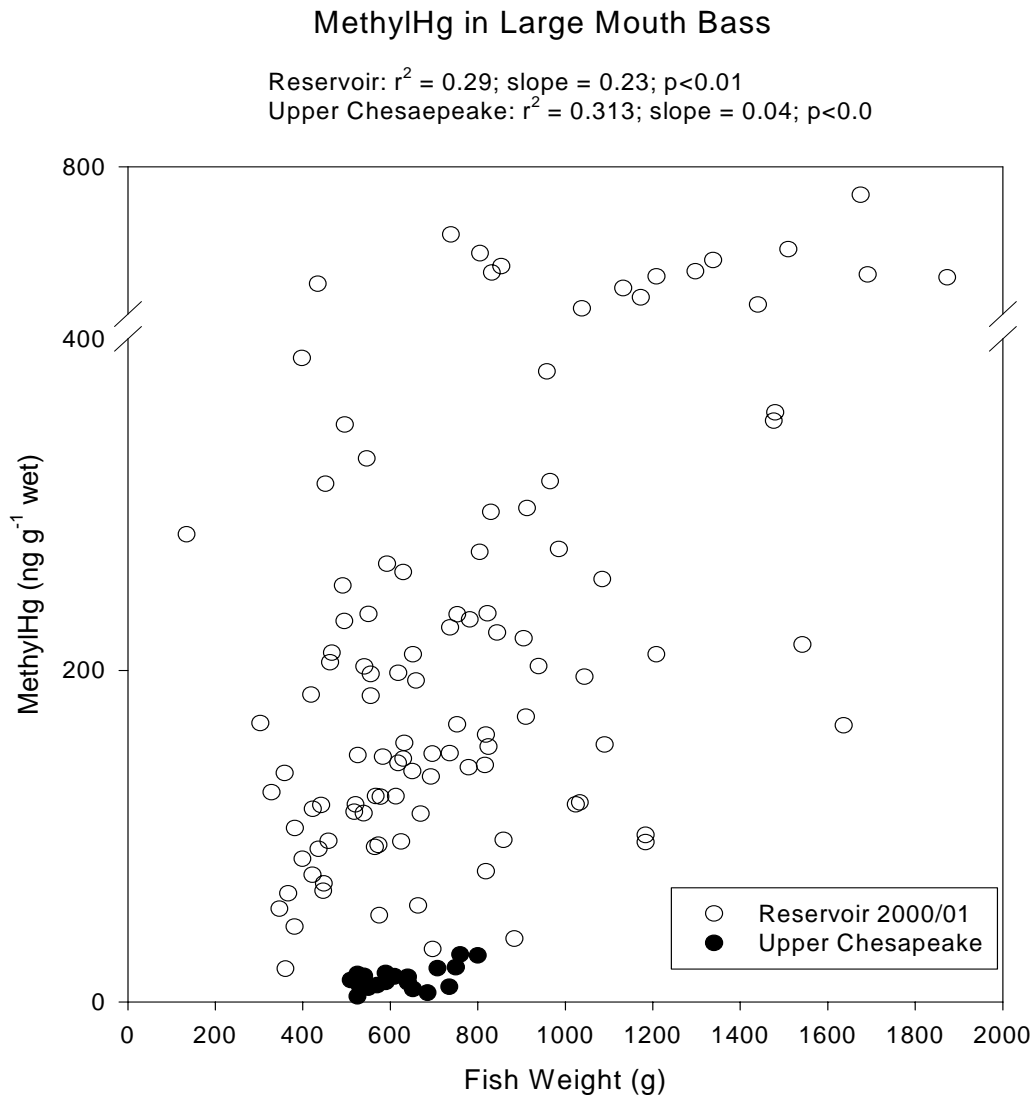Upper Chesaepeake: $r^2$ = 0.313; slope = 0.04; p<0.0



Figure 3.3. Concentrations of methylmercury (MeHg) in largemouth bass caught in the Chesapeake Bay tidal fresh reaches and in the reservoirs in Maryland. Concentrations on a wet weight basis, are plotted against fish weight.

Gilmour (1999) reported total Hg concentrations for LMB caught in the Potomac and Patuxent Rivers in 1995 and 1996. These data are for larger fish (weight-wise) and show a higher slope for the relationship between fish weight and total Hg concentration (Table 3.2). A comparison of the earlier and more recent datasets could be made if it is assumed that all the Hg in the LMB is MeHg. This is indeed the case for the reservoir fish and should be so for the estuarine fish although there is no data to support the contention. As discussed below, there is accumulating evidence that fish in different locations can have substantially different ratios of MeHg to total Hg in their muscle tissue, contrary to what is often assumed for predatory fish. Indeed, as shown above, STB have a varying relative proportion of MeHg in their muscle tissue. The slope of the line for the Gilmour total Hg data for LMB is about a factor of two higher than that of the Upper Bay fish for MeHg, and about a factor of four lower than the reservoir fish (Table 3.2). These differences will be discussed in more detail below.

Table 3.2. Regression data for largemouth bass collected in the Chesapeake Bay and in the reservoirs of Maryland.

| Sampling Location and Time | Regression Slope (ng  $g^{-1}$) $g^{-1}$ | Regr. Coeff., $r^2$ | Significance |
|---|---|---|---|
| **Methylmercury** | | | |
| Maryland Reservoirs 2000-2001 | 0.38 | 0.29 | <0.01 |
| Upper Chesapeake 2002 | 0.04 | 0.31 | <0.01 |
| **Total Mercury** | | | |
| Patuxent/Potomac Rivers 1994/1995 | 0.10 | 0.31 | <0.05 |

A comparison between the concentration of MeHg in the reservoir LMB with that of the estuarine LMB shows that, on average, the concentration in reservoir LMB is about 3-5 times greater than that the estuarine fish. Furthermore, the slope of the relationship for the reservoir fish (slope = 0.38 (ng $g^{-1}$) $g^{-1}$) is greater and thus the disparity increases with fish weight. Whether this is due to differences in growth rates and feeding patterns between the two types of ecosystems or due primarily to differences in exposure concentration is not clear. The concentration of MeHg in the waters of the reservoirs is generally higher than that of the estuary (Sveinsdottir, 1999; Mason et al., 1999) and thus the differences could be ascribed to differences in the exposure regime. Concentrations of MeHg in estuarine waters are typically <0.1 ng/L while concentrations in the reservoirs ranged up to 0.4 ng/L (Mason and Sveinsdottir, 2003). Thus, there can be up to an order of magnitude difference in MeHg concentrations and this could mostly account for the differences observed. The slopes for the relationship between weight and MeHg concentration however varied greatly between reservoirs from being very low (<0.1 (ng $g^{-1}$) $g^{-1}$) to nearly 1 (ng $g^{-1}$) $g^{-1}$. Thus, the estuarine data is at the lower end of the variability for freshwater bodies.

3.2.3 White Perch. For the WHP, the populations sampled had somewhat different concentrations with the fish from the Choptank River having higher and more variable MeHg concentrations than the Severn River (Fig. 3.4a). All the fish shown in Fig. 3.4a

were analyzed as individuals for MeHg under this project, although some of these fish were not collected by DNR personnel but by MDE. The fish from the Patapsco had intermediate concentrations although they were more similar to those of the Choptank fish. Only the dataset for the Severn resulted in a statistically significant relationship ($r^2 =$ 0.45; slope = 0.090 (ng g$^{-1}$) g$^{-1}$). Of all the WHP analyzed, the highest relative MeHg concentrations were found in fish from the Eastern Shore rivers (Fig 3.4a). The Potomac River also had some fish with relatively higher concentrations.

The MeHg concentrations are relatively low for all the datasets (<120 ng g$^{-1}$ wet weight) and this is possibly due to the relatively small size of the fish relative to the STB and LMB. However, the WHP don't attain a similar size to the other species. For all the fish species examined here, MeHg concentrations are generally in the <100 ng/g wet weight range for fish <500 g in weight. However, comparison of the slope of the concentration-weight relationship for the WHP and the STB shows that the rate of increase in concentration per gram of tissue is higher for the WHP than for the STB.

Again, WHP were also analyzed by Gilmour (1999) for total Hg - fish were from the Patuxent mostly with one fish from the Severn River. These data can be compared with the total Hg data for the Patapsco River fish (Fig. 3.4b) as these were the only samples analyzed for both total Hg and MeHg in this study. While the WHP from the Severn was larger than the current fish at 340g, its concentration was low (63 ng g$^{-1}$) and this fits with the Potomac River dataset and the 1994 Paxtuxent River data, except for the one outlier – a fish with over 400 ng g$^{-1}$ total Hg. As mentioned earlier, seasonally the mid and upper bay salinities may be low enough that there is the potential for migration of WHP between sub-estuaries and therefore they may all represent the same population, except for the Patuxent River fish.

The Patuxent River fish are likely a different population but there is no clear difference overall between the various populations in total Hg concentration. The data for WHP, although limited, indicate a relatively low %MeHg in these fish (Fig. 3.4c). This was unexpected and may reflect the fact that these smaller fish are not piscivorous but have a large proportion of their diet being invertebrates. This is not unexpected based on their known feeding preferences.

There is very little data in the literature on the fraction of total Hg as MeHg in WHP and STB, species that belong to the same genus. However, from the data presented here it appears that both species have a relatively low fraction of the total Hg as MeHg, a fraction that belies their trophic status especially for STB. While this is purely speculative, perhaps there is something about this genus that has resulted in them having the ability to effectively demethylate MeHg or in some other fashion convert MeHg taken up in their diet into inorganic Hg. Overall, it is not expected that fish have the ability to demethylate MeHg to any significant degree, especially within their muscle tissue. Research should be focused on this topic. Alternatively, this information may reflect a shift in STB bass in more recent years. Griffin and Margraf (2003) note that, compared to the 1950's, small STB are relying more on invertebrate prey and larger fish are feeding more on small pelagic prey, such as Bay anchovy. A recent report in the Bay Journal (Blankenship, 2004) indicates that large STB feeding may indeed be depleting stocks of smaller fish such as menhaden and that lack of food may be one reason for the poor condition of some STB in the Bay. Changes in prey could possibly account for the differences between the 2003-04 fish concentration and those caught in the 1990's, and

perhaps the change in diet could account for the lower fraction as MeHg in the STB. More research is required to answer this question.
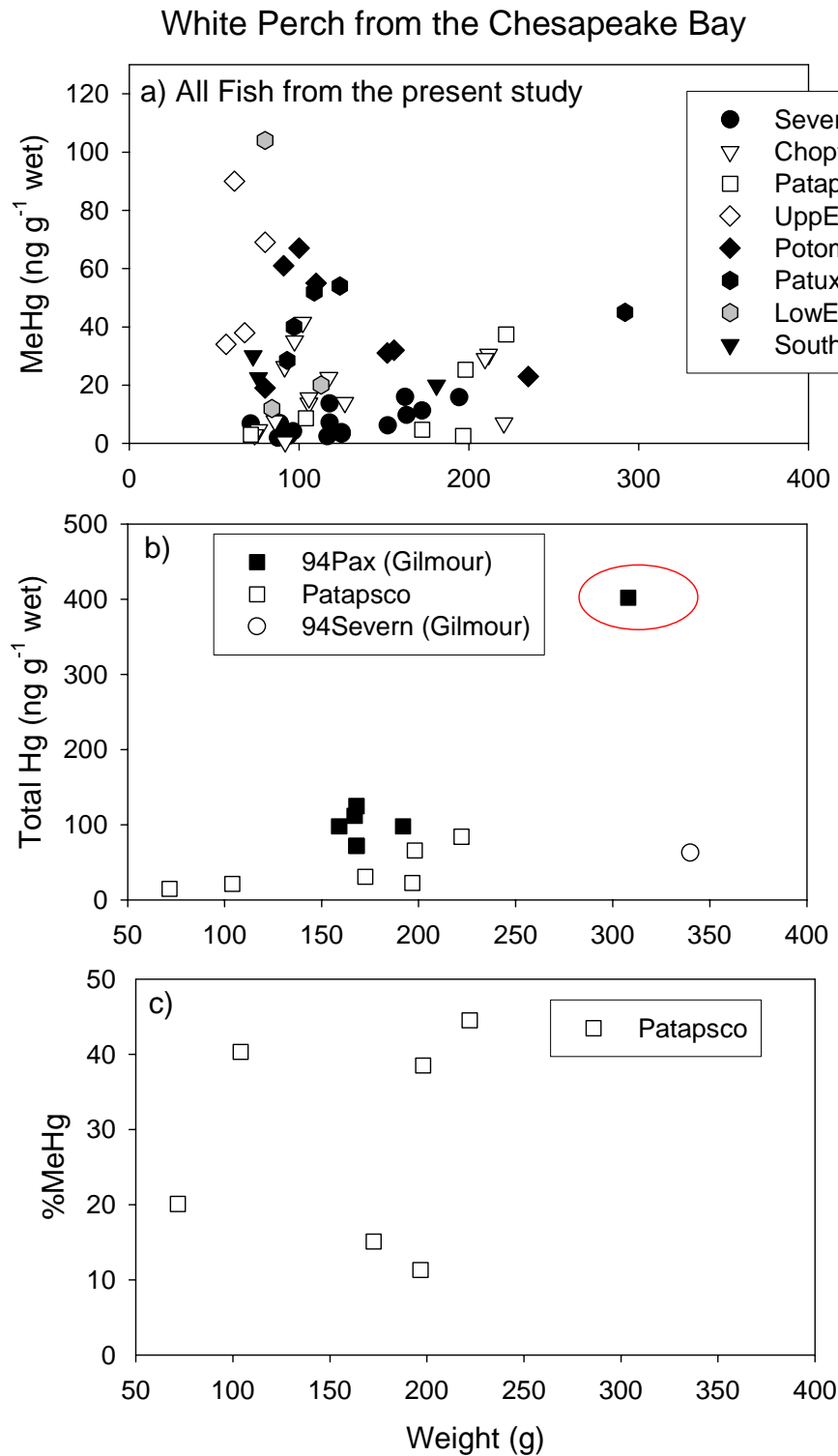


Figure 3.4: The relationship between white perch muscle tissue concentration and fish weight. a) for methylmercury (MeHg); b) for total Hg; and c) for %MeHg.

3.2.4 Comparison Between Species. It is often difficult to compare amongst species in terms of MeHg concentrations as the fish vary substantially in size. In terms of health risk, the size of the fish consumed is not relevant for the different species and thus concentration is the most useful metric. However, in terms of understanding the accumulation of MeHg in fish across habitats and species it is likely better to consider the slope of the regression line for the relationship between age, or the age proxy (weight or length), and the MeHg concentration. This provides a measure of the rate at which MeHg is being accumulated as the fish ages. Of course, the relationships between fish length, weight and age are not linear so there is some limitation to the usefulness of this approach. However, it is clear from the data presented here that none of the estuarine fish species (STB, LMB and WHP) are accumulating MeHg at rates (all species, slope <0.1 (ng g$^{-1}$) g$^{-1}$) comparable to that of the reservoir LMB (0.38 (ng g$^{-1}$) g$^{-1}$ on average). Such differences can be to a large degree explained by differences in MeHg water concentrations which were overall higher for the reservoirs (0.01-0.4 ng L$^{-1}$) than in the Bay (see below; 0.01-0.1 ng L$^{-1}$) but other factors must also be important. As discussed by Mason and Sveinsdottir (2003), the LMB fish MeHg concentration in the reservoirs was most strongly related to MeHg levels in the water, although other variables were also important.

It is generally assumed that essentially all the Hg in fish muscle tissue is MeHg and this assumption is primarily based on an early study by Bloom (1992). However, there is evidence in the literature that this is not always the case and a number of recent publications have shown this not to be true, especially for estuarine and coastal fish (Baeyens et al., 2003; Riget et al., 2000; Kannan et al., 1998; this work). Kannan et al. (1998) examined the concentration of Hg and MeHg in numerous fish species in South Florida estuaries and found low fractions of MeHg in catfish (56-100% MeHg) and spot (54-100%). Most other fish species had >80% MeHg. Baeyens et al. (2003) showed that species resident in the Scheldt estuary had lower %MeHg concentrations in their tissue than coastal and North Sea fish of the same species (Table 3.3). For example, the %MeHg in plaice decreased from about 97% for North Sea fish to 84% for Belgium coastal fish to 64% for fish from the Scheldt estuary. In addition, the MeHg concentration was lowest in the Schedlt estuary fish even though this is considered to be a relatively polluted river (Baeyens et al., 2003). It is likely that the differences %MeHg reflect differences in feeding preferences. A similar trend was seen for the other species. Thus in terms of this study, the results found for STB for %MeHg are reasonable.

A detailed study by Holsbeek et al. (1997) showed that a variety of relationships exist between fish size and Hg and MeHg content. For the majority of species, there is an increasing level of MeHg in tissue with increasing age, with an overall low and relatively constant inorganic Hg burden. So, for these fish essentially all the muscle tissue is MeHg, regardless of age. Or, alternatively, the fraction as MeHg increases with age. However, for some species, there appeared to be a relative increase in inorganic Hg relative to MeHg with age, such that the % MeHg decreased with age. This was found here for the STB. However in the study of Holsbeek et al. (1997) this pattern was only found with two planktivorous fish (*Hilsa* and *Ilisha*). However, such trends have also been reported for large open ocean fish such as blue marlin, and other species from the Northern Barents Sea (as reported by Holsbeek et al. (1997)). For these studies, the potential for locally high inorganic Hg inputs were ruled out as an explanation for the

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relatively high inorganic Hg content.  Kannan et al. (1998) found a weak correlation (r = 0.24; p<0.1) between % MeHg and total Hg for the fish species they examined from the Florida estuaries.  Both fish total Hg and MeHg were consistent with sediment total Hg and MeHg indicating a link between sediment and fish tissue in this instance.

In another study, Riget et al. (2000) found that the fraction of MeHg in Arctic char varied strongly between land-locked resident populations (91.5 ± 2.1 %) and anadromous fish (72.3 ± 2.0%). Here the migratory fish had a much lower MeHg concentration (median size adjusted values for different lakes of 0.023-0.080 ng g$^{-1}$) than the resident fish (0.13-0.67 ng g$^{-1}$). This trend is similar to what was found in this study in that the estuarine LMB had a lower MeHg burden than the reservoir fish (Table 3.4). With the Arctic char, there was a distinct difference in the rate of growth of the fish with resident populations, ranging in size from 24-48 cm, being 11-19 years old compared to the estimated age of anadromous fish of 36-40 cm, of 6-7 years. Clearly, the slower growing land-locked fish were accumulating relatively more MeHg than the faster growing migratory fish. It is also possible that differences in food source may account for the differences in fish MeHg concentration rather than differences in growth rate.

The likelihood of a demethylation process being present in these fish is intriguing but the species for which such patterns in inorganic Hg and MeHg concentration have been found cover a wide range of species and different locations and is therefore somewhat difficult to reconcile.  Further research is clearly needed to examine the potential for MeHg demethylation by fish.  However, it is clearly obvious that measurements of only total Hg in fish are inadequate if risk based on MeHg is to be evaluated.

Table 3.3. Data on the speciation of mercury in fish caught in the Scheldt estuary, the Belgium coastal zone and in the North Sea. Taken from Baeyens et al. (2003).

| Species | Location | n | Total Hg (ppm) | MeHg (ppm) | %MeHg |
|---------|----------|---|----------------|------------|-------|
| Flounder | Scheldt | 14 | 0.084 ± 0.03 | 0.056 ± 0.02 | 67 |
| Flounder | Coastal Zone | 24 | 0.13 ± 0.06 | 0.11 ± 0.06 | 82 |
| Plaice | Scheldt | 3 | 0.031 | 0.020 | 64 |
| Plaice | Coastal Zone | 13 | 0.063 ± 0.02 | 0.053 ± 0.02 | 84 |
| Plaice | North Sea | 17 | 0.045 ± 0.02 | 0.043 ± 0.02 | 97 |
| Dab | Coastal Zone | 11 | 0.069 ± 0.02 | 0.057 ± 0.02 | 83 |
| Dab | North Sea | 13 | 0.101 ± 0.05 | 0.098 ± 0.05 | 97 |
| Whiting | Coastal Zone | 19 | 0.11 ± 0.03 | 0.097 ± 0.03 | 87 |
| Whiting | North Sea | 5 | 0.10 ± 0.02 | 0.091 ± 0.02 | 91 |

Similar reasons to those discussed above may account for the lower concentrations of MeHg in the estuarine LMB, and for the relatively low concentration and rate of accumulation in the STB and WHP (Figs. 3.1-3.4; Table 3.4). While there is no growth data available for the estuarine LMB, the length-weight relationship of the fish caught in 2002 and those reported by Gilmour and Riedel (2000), and some earlier literature values (Hildebrand and Schroeder, 1928), are plotted against the data for the

reservoirs obtained by Mason and Sveinsdottir (2003) and by Mark Castro for Piney Run Reservoir (taken from Mason and Sveinsdottir, 2003) (Fig. 3.5).

Table 3.4. Concentration of methylmercury on a wet weight basis for fish recently caught in Maryland waters. All samples were analyzed at CBL under this project, during previous MD DNR funded studies (Mason and Sveinsdottir, 2003), and from samples collected by MDE (unpublished data) and by this research group (unpublished data), and other sources (Mason and Lawrence (1999).

| Common Name | Size (inches) | MeHg (ng g$^{-1}$ wet ) | %MeHg | # of fish | Ref. |
|---|---|---|---|---|---|
| **Vertebrates** | | | | | |
| Largemouth Bass- Reservoir | 12 - 22 | 310 ± 290 | 95 ± 35 | 225 | 1 |
| Smallmouth Bass | 12 - 17 | 360 ± 160 | 91 ± 25 | 18 | 1 |
| Striped Bass | 15 - 42 | 120 ± 100 (9 – 530) | 73 ± 37 | 79 | 2 |
| Channel Catfish | 14 - 30 | 13 – 21 | - | 20* | 3 |
| White Perch | 7 - 10 | 2 – 104 | 28 ± 14 | 21** | 2,3 |
| Crappie - Reservoir | 6-12 | 90 ± 60 | 83 ± 45 | 49 | 1 |
| Bluegill - Reservoir | 5 - 10 | 70 ± 80 | 80 ± 36 | 97 | 1 |
| Carp | ~ 20 | 26 | - | 1* | 3 |
| Largemouth Bass - Estuarine | 15 – 18 | 14 ± 7 | - | 16 | 2 |
| Yellow Perch | ~ 10 | 13 | - | 1* | 3 |
| Eel | ~ 20 | 10 | - | 1* | 3 |
| Anchovy | | 4-8 | | 3* | 4 |
| **Invertebrates** | | | | | |
| Blue Crab | | 2-11 | 55 ± 19 | 5 | 3 |
| Clams | various | <1-2 | <5 | many | 5 |
| Copepods | >202 µm | 1-4 | - | 5* | 4 |
| Amphipods | | <1-3 | | mixed | 5 |

References: 1 = Mason and Sveinsdottir (2003); 2 = Data from this study; 3 = fish analyzed by MDE, unpublished data; 4 = samples collected and analyzed by this research group, unpublished data; 5 = clams collected in the vicinity of Hart-Miller Island and data from Mason and Lawrence (1999). Note that earlier data from Gilmour (1999) is not included here as no methylmercury measurements were made in that study.
*The number represents the number of composite samples of 1-5 fish, or invertebrates
**The data are a combination of 21 composite samples of 1-5 fish, and 30 individual fish

It is clear that the Upper Bay 2002 LMB represent a different population in that for a fish of a particular length, the weight is lower than those of all the other datasets. This suggests that this population of LMB is growing at a different rate to the reservoir and Patuxent and Potomac populations, which all appear to have similar weight-length relationships. Indeed, when comparing the rate of increase in MeHg concentration in terms of length rather than weight for the LMB, there is much less difference between the data collected in 2002 and the 1995-96 data of Gilmour and Riedel (2000). By inference,

based on the Riget et al. (2000) data, one could also conclude the estuarine LMB may have a lower fraction of the total Hg as MeHg compared to the reservoir fish. Such a notion is consistent with the data of this study and of Gilmour (1999).
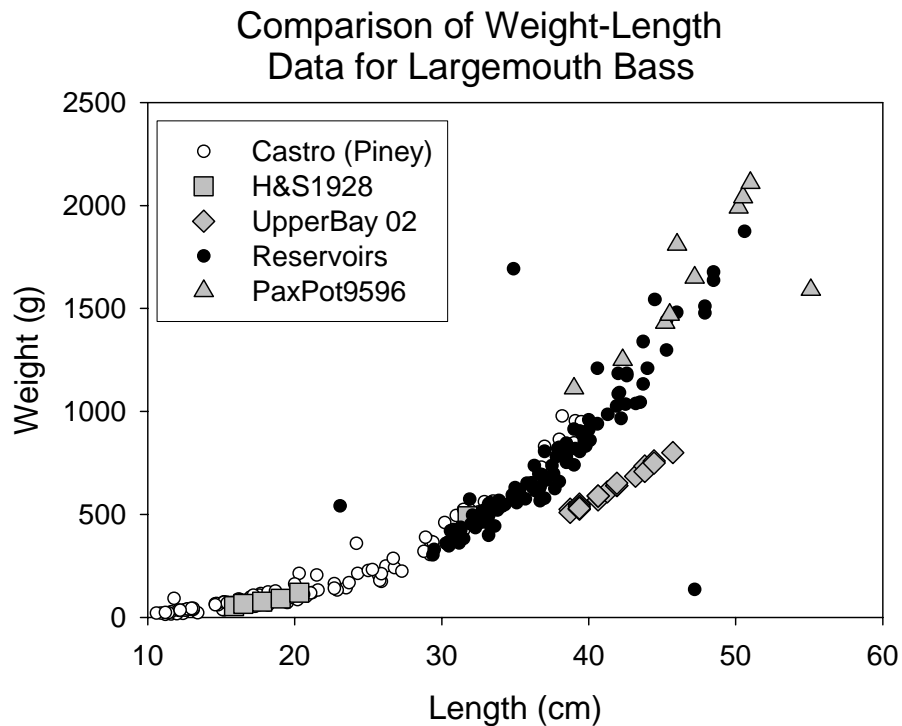


Figure 3.5. Relationship between largemouth bass weight and length for different groups of fish caught in various reaches of the mainstem Chesapeake Bay and its tributaries, as well as in the reservoirs. See text for details.

*3.3 Total Mercury and Methylmercury and Ancillary Parameters in Water and Sediment*
      3.3.1 Water. Total Hg concentrations have been measured in the surface waters of the Chesapeake Bay mainstem and in the various tributaries on a number of occasions. Samples were also collected in the lower Bay and Potomac River in February and July 1997 (Table 3.5). Additionally, samples have been collected in the Patuxent River (Benoit et al., 1998) and in the Anacostia River (Mason and Sullivan, 1997), which flows into the Potomac near Washington, DC. Total Hg concentrations were generally <3 ng/L except at locations close to urban centers (e.g., Baltimore Harbor, the Anacostia-Potomac confluence; Table 3.5). A substantial fraction of the Hg in the water was associated with suspended particulate matter (SPM). Particulate Hg concentrations were not measured on all samples but our measurements in other associated studies within the Chesapeake Bay system (Lawson et al., 2001a, 2001b) show that, while the distribution coefficient for Hg between dissolved and particulate phases (log $K_d$) is a function of SPM, the change is relatively small over the SPM concentration range found within the mainstem Bay (5-30 mg/L). For example, in the Anacostia River, Mason and Sullivan (1997) found that the log $K_d$ decreased, on average, from around 5.3 at 5 mg/L SPM to 4.9 at 30 mg/L, a factor of 2-3 decrease, and that the organic content of particulate (%POC) was a better predictor

of log $K_d$ than SPM. In the Patuxent River, Benoit et al. (1998) found a similar range in log $K_d$ values (4.8-5.7) for comparable SPM and these values are similar to those determined by others (e.g., Cossa et al., 1996). The observed decrease in log $K_d$ with increasing SPM has been noted by others (e.g., Honeyman and Santschi, 1988) and has been attributed to the presence of colloidal material in the so-called "dissolved" (filter-passing) fraction. It is probable that this accounts for the changes seen here and also accounts for the relationship with POC as the relative amount of Hg-binding colloidal material is related to the overall organic content of the water.

Table 3.5: Concentrations of total mercury and methylmercury in water from various regions of the Chesapeake Bay.

| Location | Total Hg (ng/L) | MeHg (ng/L) |
|---|---|---|
| Conowingo Dam Outlet | 1.8 ±1.6 | 0.05 ± 0.06 |
| Upper Bay | 4.0 ± 3.0 | 0.03 ± 0.02 |
| Mid Bay | 0.45 ± 0.03 | 0.09 ± 0.02 |
| CBL | 1.1 ± 0.98 | -- |
| Potomac River Mouth | 1.3 ± 0.70 | 0.01 |
| Potomac River at Little Falls | 2.0 (low flow) | 0.04 (low flow) |

The concentration of total Hg in the mainstem Bay was highest in the northern Bay (Table 3.5), where the concentration was typically between 3 and 4 ng/L, and decreased down-estuary to typical values of less than 2 ng/L at the mouth of the Patuxent (Benoit et al., 1998) and Potomac Rivers.  The average concentration of total Hg in the Susquehanna River, the main tributary source to the Chesapeake, was not greater than that of the upper Bay (Lawson et al., 2001a).  The salinities in the upper Bay range from 2-8 ppt, depending on river flow, and thus, given that seawater has a lower Hg concentration than the river water (Cossa et al., 1996; Mason et al., 2001), the measured Hg concentrations in this region cannot result purely from water mass mixing, i.e., river input is not the only source of Hg to this section of the Bay.  Atmospheric input is also important (Mason et al., 1999).

The longer-term collections at the Conowingo Dam, at the Chesapeake Biological Laboratory's research pier and additional monthly collections on the Potomac and other rivers at the "fall line" locations provide an indication of the variability in riverine concentration (Lawson et al., 2001a).  The flow-concentration relationship for total Hg in the tributaries showed an increase in concentration under high flow conditions (Lawson et al., 2001a; Mason et al., 1999). Under baseflow conditions, concentrations were typically less than 2 ng/L.   Collections on each of the rivers made during storms showed elevated concentrations (up to 12 ng/L).  A strong relationship between flow and total Hg concentration has also been found in smaller, forested streams in Western Maryland (Lawson et al., 2001b) and in the Anacostia River (Mason and Sullivan, 1998). Additionally, high concentrations in the Patuxent River were found under storm conditions in February 1996 (Benoit et al., 1998; up to 12 ng/L total Hg). The longer term record at CBL and at the Conowingo Dam (Table 3.5), while not specifically targeting storm flow, did show high concentrations on occasion, and gives an indication of the temporal variability in concentration.

Methylmercury concentrations of surface waters of the Chesapeake Bay were generally low, as has been found in other estuarine and freshwater systems (Benoit et al., 1998; Mason et al., 1993; Leermarkers et al., 1995; Cossa et al.; 1996, Baeyens et al., 1996). The values for the mainstem and tributaries of the Chesapeake Bay were somewhat lower than those of the upper tributaries (Table 3.5). In the Patuxent River, Benoit et al. (1998) found concentrations of less than 0.05 ng/L for the saline portions of the estuary. As found in other estuarine systems, concentrations can be elevated in the low oxygen bottom waters that develop in summer as found, for example, in the Pettaquamscutt estuary (Mason et al., 1993). The highest concentrations of MeHg in the water column were within the redox interface with low concentrations in the surface waters. Concentrations were also elevated in the anoxic bottom waters. Similar profiles for MeHg have been seen in seasonally anoxic lakes (e.g., Bloom et al. 1991; Watras et al., 1996). In these circumstances, MeHg concentrations are typically a higher fraction of the total Hg than in surface waters. The mixing of low oxygen waters to the surface could be an important pathway for the exposure of water column biota to MeHg, as has recently been shown for seasonally stratified lakes which develop anoxic hypolimnia (Herrin et al., 1998; Slotton et al., 1995). Such mixing could elevate MeHg concentrations in the mainstem Chesapeake Bay in fall, but this has not been documented.

Concentrations of MeHg were also measured in the tributaries (Table 3.5). Results suggest that concentrations in the rivers were less than 0.05 ng/L generally under baseflow conditions but increase under high flow to values above 0.2 ng/L. The relative increase was less than that for total Hg, and there was an exponential decrease in % MeHg with increasing flow (Mason et al., 1999). Overall, the % MeHg under baseflow conditions was similar to that of the mainstem Bay.

Given the overall similarity in concentration of MeHg across the Bay, and the high variability at any one location, it is not possible to conclusively determine whether concentration differences are a major factor in contributing to differences in fish MeHg concentration between fish caught at different locations. This is especially true for the STB given their high mobility. However, it is clear that concentrations of MeHg in the mainstem Chesapeake Bay are generally much lower than those of MD freshwaters, by as much as a factor of 5-10. The range of such differences is equivalent to the differences in LMB MeHg concentrations between freshwater and estuarine fish. Thus, as found in the previous studies, MeHg content in water influences to a large degree fish MeHg burdens. Other factors such as pH are less important in the estuarine/coastal environment as the system is well-buffered. Additionally, except for the upper estuarine reaches, the DOC content of the waters is relatively consistent.

Measurements of DOC in the Upper Bay found concentrations of DOC in the range of 1.8 – 4.2 mg/L, which are similar to those of the Susquenhana River (Mason et al., 1999; Rochelle-Newall and Fisher, 2002). Distributions down the mainstem Bay followed a mixing line indicative of the mixing of higher concentration freshwaters with lower DOC (< 8 mg/L) coastal waters. At the mouth of the Chesapeake Bay (~30 ppt), concentrations ranged from 8 – 12 mg/L (Rochelle-Newall and Fisher, 2002). This range in DOC is much less than that found across freshwater ecosystems, such as the MD reservoirs (range of 16 – 50 mg/L) (Mason and Sveinsdottir, 2003). Thus, the impact of DOC on bioaccumulation will be less apparent for the estuarine fish.

Chloride concentrations were one parameter found to be potentially important for the reservoir LMB. However, the STB and WHP investigated here move within the salinity gradient and therefore any impact of salinity will be masked. As sulfate levels generally track salinity, the same conclusion can be reached for this parameter. Thus, overall, it is not possible to assess the impact of ancillary parameters given the small variability (pH, DOC) or the confounding nature of the fish movement.

3.3.2 Sediment. The concentration of Hg in sediments ranged from higher concentrations in and near Baltimore Harbor to lower values in the mainstem Bay (<100-200 ng $g^{-1}$; Figure 3.6; Mason and Lawrence, 1999). The average suspended particulate concentration of the Susquehanna, based on measured SPM and Hg concentrations, is 250 ng $g^{-1}$ (Lawson et al., 2001a) and values for the mainstem Bay and the tributaries are typically less than 300 ng $g^{-1}$, suggesting the importance of sediment loading from the rivers in contributing to the overall Hg sediment burden of the Bay. Mason et al. (1999) concluded that the sedimentary input from the Susquehanna and the other tributaries was of the same order as the amount of Hg being buried in the sediments of the mainstem Bay. The MeHg in sediments of the mainstem Chesapeake Bay were low (<2 ng $g^{-1}$) compared to other sites, such as Baltimore Harbor (Mason and Lawrence, 1999). Values did not decrease down the mainstem in a similar fashion to total Hg (Fig. 3.6), suggesting that *in situ* conditions, rather than river sources, are the most important source for MeHg in the mainstem Bay. Mason et al. (1999) concluded from their mass balance evaluation that most of the MeHg within the Bay ecosystem was contributed via net *in situ* production, from their mass balance evaluation.

Studies with Baltimore Harbor sediments, and using long-term mesocosm studies, suggest that methylation of Hg is occurring in the estuarine sediments (Kim et al., 2004). The fraction of the total Hg as MeHg does not decrease generally down the Bay (Fig. 3.6). This is not what would be expected given the higher salinity of the lower Bay (Benoit et al., 2003) and the potential inhibition of methylation in the presence of increased sulfide. However, as the inflowing waters from the coastal zone likely contain labile organic carbon and because *in situ* primary productivity is highest in the mid to lower Bay, the contrasting effects of sulfide inhibition and increased microbial activity likely counteract each other. In addition, the high Fe content of these sediments potentially mitigates sulfide buildup by precipitating Fe-S solid phases. Indeed, the % MeHg in Chesapeake Bay sediments is higher than other similar estuaries that have been studied, for example the Hudson River (Heyes et al., 2004). The relatively high % MeHg in sediments and the relative shallowness of the Bay overall suggests that this MeHg is likely incorporated into the food chain through physical processes such as sediment resuspension and release from sediments, and through accumulation into benthic and pelagic organisms which are fed on by the Bay fish, such as WHP and STB.

A study of the release of Hg and MeHg from sediments of Baltimore Harbor (Mason et al., submitted) concurred with other previous work (e.g., Gill et al., 1999) that the flux of MeHg from sediments to the water column is enhanced under conditions of low water column oxygen/hypoxia. Under these conditions it is likely that, at the sediment surface, reduction of iron oxides and other oxidized phases is releasing MeHg into the water column. In contrast to such conditions, there is the potential for uptake of inorganic Hg by reduced sediments, likely due to precipitation of sulfide phases. Thus, in the mainstem Chesapeake Bay, summer low oxygen conditions could be enhancing the

release of MeHg from sediments. Indeed, higher concentrations of MeHg were measured in low oxygen bottom waters of Baltimore Harbor (Mason et al., 1999), as expected based on the above discussion. Therefore direct release from sediments is a likely important mechanism for MeHg transfer to fish. Additionally, sediment resuspension can provide another pathway for the effective transfer of MeHg from sediments to filter-feeding organisms (Kim et al., 2004; in review).
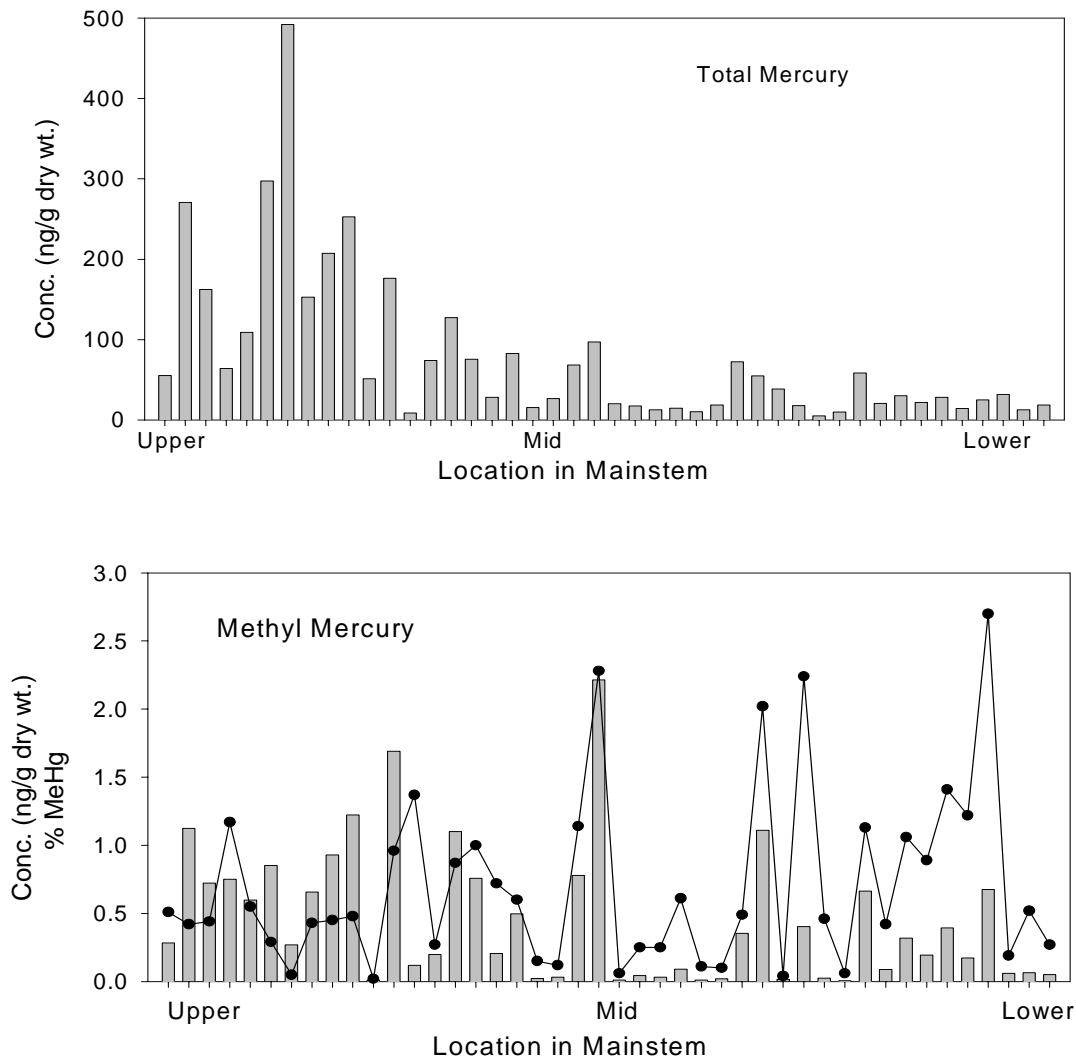


Figure 3.6: Concentration of a) total mercury (Hg) and b) methylmercury (MeHg; bar), as well as percent methylmercury (%MeHg; line), in sediments of the mainstem Chesapeake Bay. Sample locations are distributed throughout the Bay from the mouth of the Susquehanna River to the lower Chesapeake Bay.

*3.4  Otolith Chemistry and Methylmercury in Striped Bass*

The incorporation of elements into fish otoliths, which are essentially calcium carbonate ($CaCO_3$), occurs with the incorporation rate being related to water chemistry in some instances, while in other cases there is no relationship (Secor et al., 2001). Strontium (Sr) is one element that is incorporated into the otolith lattice. Ocean Sr:Ca molar ratios in water are between 8.5-9 mmol mol^{-1} and freshwater values tend to be much less (typically <5), although they can be highly variable (Kraus and Secor, 2004). In a detailed study of STB in the Hudson River, Secor et al. (2001) determined that the Sr:Ca ratio of otoliths was a reliable indicator of the STB life history.  Fish that spent the majority of their lives in the open ocean, only returning to the estuary yearly to spawn, had the highest ratio, on the order of 6 to 6.5 mmol mol^{-1}.  This molar ratio is similar to that of seawater.  On the other hand, Secor et al. (2001) found that resident STB in the Hudson River had Sr:Ca in otoliths of <2, with an average of 1.4 mmol mol^{-1}, which is determined to be equivalent to an average salinity of 2 ppt.  Fish that inhabited the mesohaline Hudson River and did not migrate offshore had Sr:Ca in otoliths of 4 – 5.4, which is deemed equivalent to salinities of 13 to 20 ppt.  It would be expected that STB in the Chesapeake Bay would show similar variability.

There is variability in the Sr:Ca values for different rivers, however, and this could limit the usefulness of the proxy if the river concentration is elevated and near that of seawater (Kraus and Secor, 2004). Indeed, these authors noted that the Choptank River is one local environment with a Sr:Ca ratio relatively similar to that of seawater (at Greensboro, average ratio is 4.9 mmol mol^{-1}; USGS data). For the Susquehanna River, measurements at the Conowingo Dam show a range of values from 2.5-3.5, with an average of 2.8 mmol mol^{-1}. Indeed, otoliths of LMB from the Upper Bay were analyzed under this project and the values fall within this range, from 1.4 to 4.0, with an average of 2.45 $\pm$ 0.52 mmol mol^{-1}. For other major tributaries, the ratio varies between 2 and 3 mmol mol^{-1} (Patuxent at Bowie 2.2; Potomac at Chain Bridge 2.4; Rappahannock at Fredericksburg 3.1 mmol mol^{-1}).

Thus, STB that predominantly inhabit the mid-to upper Bay region, and do not migrate offshore, should have otolith Sr:Ca values of 3 mmol mol^{-1} or less, except if they inhabited the upper reaches of the Choptank River for extended periods, while the fish that spent extended periods offshore would have ratios of 6 mmol mol^{-1} or greater.  The Sr:Ca ratio was measured in a number of otoliths taken from STB sampled in 2002 at Deale and Point Lookout and in spring 2003. The data are plotted in Fig 3.7 against the fish weight and the fish MeHg concentration. A three-way plot in Fig. 3.7c shows the relationship between these three variables for the STB caught at different times and different locations. For the fish caught in 2002 there appears to be two populations in terms of Sr:Ca ratio: one with values of 2-6 mmol mol^{-1}; the other with values from 4-6 mmol mol^{-1}. The higher ratios are mostly associated with the fish caught at Deale and likely represent fish that are resident of the Upper Bay and its tributaries. As noted above, and based on the USGS data available, it appears that the rivers of the Eastern Shore, and especially the Upper Eastern Shore (Choptank and Chester Rivers, for example) have Sr:Ca ratios for their freshwater reaches of >4 mmol mol^{-1}. In contrast, the Susquehanna River has a relatively low Sr:Ca ratio of 2.8 mmol mol^{-1}. Thus, the higher ratios for these fish do not necessarily suggest that thes e are migratory fish.  Indeed, these fish are likely to be residents of the Bay.
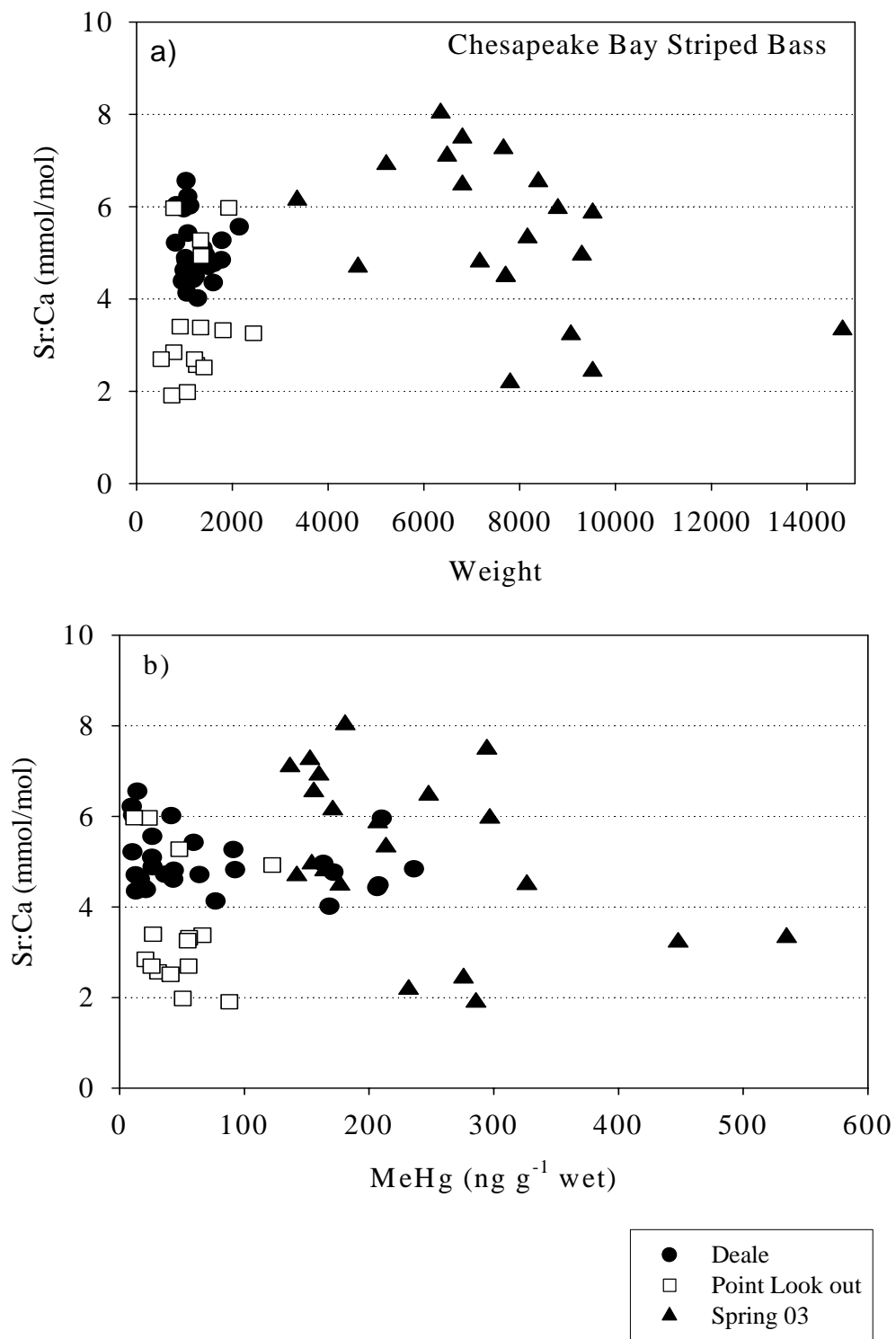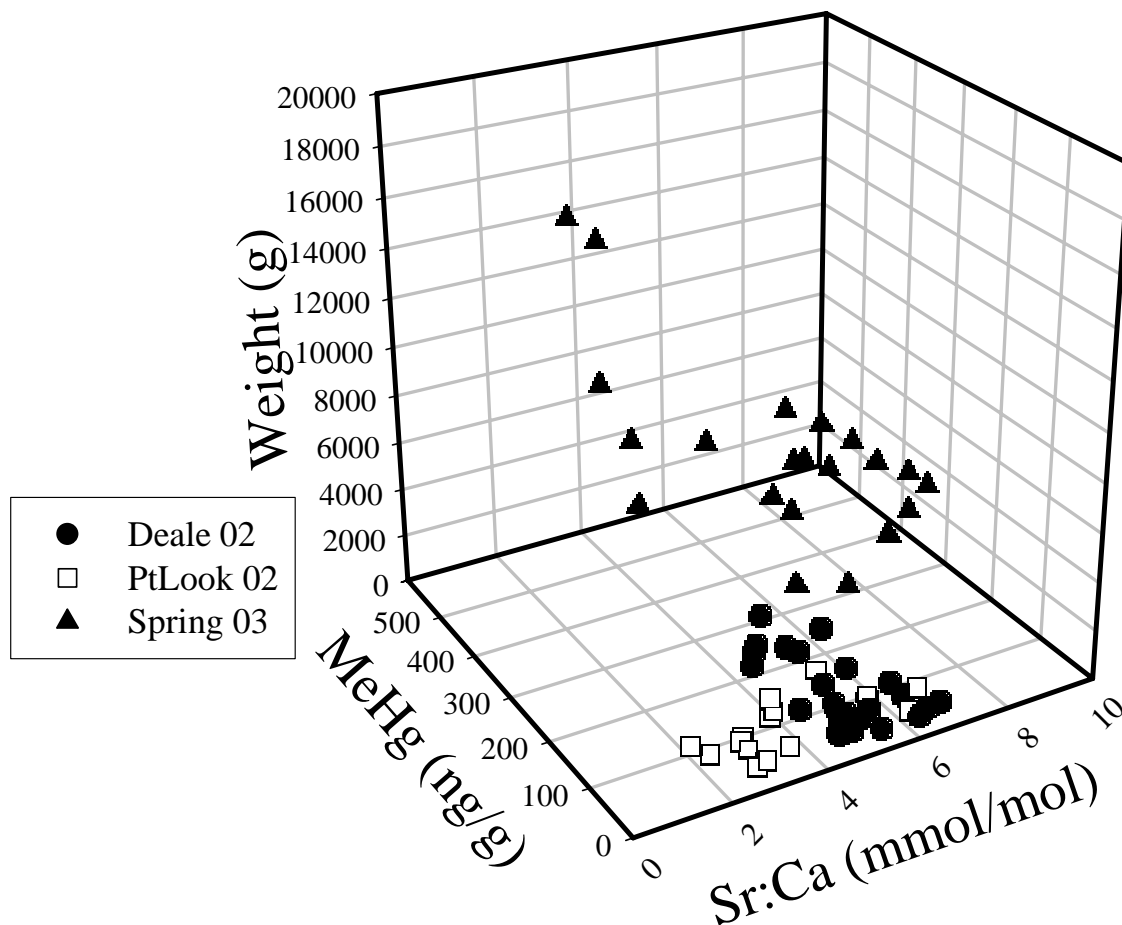
Figure 3. 7. a) The relationship between fish weight and strontium:calcium ratio (Sr:Ca) for striped bass (STB) caught within the mainstem Chesapeake Bay; b) the relationship in terms of Sr:Ca and methylmercury content (MeHg); and c) the three parameters plotted on the same graph. Diamonds represent fish caught at Deale; squares are fish from Point Lookout and triangles are fish caught in Spring 2003.

Examination of the data in Fig. 3.7a shows that the fish caught in Spring 2003, where otoliths were analyzed, were all >3 kg. However, their Sr:Ca values ranged from around 2 to nearly 8. Four of the largest fish had low values (< 4 mmol mol^{-1}) and this suggests that these were fish that resided dominantly in the mainstem Upper Bay. The fish of intermediate size, 4-9 kg, had the highest Sr:Ca ratios and these likely represent migratory fish as, even though the rivers of the Chesapeake Bay have relatively high Sr:Ca ratios, none are >5 mmol mol^{-1}. Finally, there is a group of large fish with intermediate Sr:Ca ratios which cannot be distinguished as being either resident or migratory based on the analysis performed.

The largest fish had the highest MeHg concentrations (Fig. 3.7c). The reason for this could be related to purely size-related effects as there is significant relationship between fish weight and MeHg content for STB (Fig. 3.1). The alternative explanation is that these are fish that spend relatively more of their time in the Bay than offshore, as suggested by their Sr:Ca ratio, and that they are therefore exposed to higher MeHg levels and thus contain a higher MeHg burden.

As suggested above, it would be expected that fish that spend the majority of their life offshore should have a lower MeHg burden that those that remain in the estuary, given the higher MeHg concentrations in sediment and water in the Chesapeake Bay compared to the shelf and open ocean waters (Mason et al., 1999; Mason and Fitzgerald, 1996). However, examination of Fig. 3.7b and 3.7c suggests that there is no strong evidence for this and there is little relationship between Sr:Ca and fish MeHg. These results suggest that there must be a number of conflicting factors that confound the usual relationship. Clearly, the relatively high Sr:Ca ratios, and the high variability for the tributaries of the Chesapeake Bay limit the usefulness of this technique in assessing migratory patterns.

In summary, while otolith analysis provides some indication of patterns of migration in Chesapeake Bay STB, and confirms the conclusions of Secor et al. (2001) that STB have fairly divergent life history traits, it does not provide a clear picture of higher exposure for estuarine fish. Clearly, migration is a confounding factor in determining the age-MeHg relationship as not all STB has the same life history in terms of their mobility over time. Separation of STB by sex would allow better determination of life history as larger (> 4 kg) female fish are more likely to migrate.

3.5   *Methylmercury Bioaccumulation*

The concentrations of MeHg in fish and invertebrates from the Chesapeake Bay are given in Table 3.4. Concentrations are low for small invertebrates such as copepods and amphipods (< 5ng $g^{-1}$ wet weight) (Mason and Lawrence, 1999) and thus organisms feeding on them, such as anchovies and menhaden, should have low MeHg burdens as a result. The bioaccumulation factor per trophic level for MeHg is about 3-5 (Mason et al., 1995; Watras and Bloom, 1992) so that fish feeding exclusively on  invertebrates should have MeHg burdens of <25 ng $g^{-1}$ wet weight. This is indeed the case with anchovies, which feed predominantly on copepods, having concentrations in the range of 4-8 ng $g^{-1}$ wet weight compared to their prey of 1-4 ng $g^{-1}$. Large invertebrates, such as crabs, have burdens a factor of 2-3 higher (2-11 ng $g^{-1}$), reflecting their more omnivorous, scavenging nature. In contrast to blue crabs, crayfish from the MD reservoirs had higher MeHg burdens, averaging 22 ± 14 ng $g^{-1}$ wet weight (range 7 - 45 ng $g^{-1}$ wet weight) (Mason and Sveinsdottir, 2003). Such differences lower in the food chain between the reservoirs and the estuary are consistent with the higher concentrations found, for example for LMB in the reservoirs.

For the estuarine species examined here, WHP of the size analyzed are the fish likely to be feeding on invertebrates, with their diet supplemented by small fish. Most of the fish had MeHg concentrations of < 40 (ng $g^{-1}$) $g^{-1}$, which indicates a diet mostly consisting of crabs and other invertebrates. Of the other species examined, LMB are likely feeding on mixture of invertebrates and fish. Their MeHg burden reflects this. As

mentioned above, the diet of the LMB in reservoirs had a higher MeHg burden (Mason and Sveinsdottir, 2003). Small fish in the reservoirs had MeHg levels of 9 – 45 ng g$^{-1}$ for fish <10 cm (4 inches) so that fish feeding on these fish would be expected to have a burden of up to 250 ng g$^{-1}$. Clearly, the larger LMB in the reservoirs must be feeding on larger fish. The average concentration for the LMB in this study, which ranged in size from 38-45 cm (15–18 inches) was 16 ± 7 ng g$^{-1}$ wet weight. While no stomach content analysis was done, such levels reflect a diet that must be dominated by invertebrates. If fish were the dominant food, higher concentrations would be expected based on the measured concentrations of MeHg in the various estuarine species (Table 3.4).

The larger STB feed almost exclusively on fish such as menhaden and anchovies, as discussed above and therefore, based on simple food web bioaccumulation estimations, should have MeHg levels of 200 ng g$^{-1}$ or greater. Such an estimation is consistent with the measured burdens in the fish. Clearly, as fish retain MeHg as they grow, their burden increases with age and the simple bioaccumulation factor approach is not sufficient to explain all the variability in concentration.

In summary, the concentrations of MeHg in small fish and invertebrates caught in the Chesapeake Bay are lower than those of comparable organisms from MD reservoirs. The differences are consistent with the magnitude and direction of the differences in MeHg concentrations in the water. It appears that the lower MeHg concentration in estuarine water is the primary reason why fish from the estuarine waters have relatively lower MeHg burdens.

The differences in MeHg levels in the water is not directly related to levels of Hg in atmospheric deposition as these inputs are relatively similar across the state for locations away from local inputs (Mason et al., 2000). Thus, the reservoirs either appears to be able to produce and transport more MeHg from sediments to the food chain, or the concentration differences depend on surface area/volume considerations and the relative extent of wetlands and other locations where methylation is enhanced.

3.6   *Conclusions*

1.   Concentrations of MeHg in STB caught in the Chesapeake Bay and its tributaries show a relationship with fish weight. However, fish of over 5 kg still have relatively low MeHg burdens compared to fish that inhabit MD reservoirs. Considering 300 ng g$^{-1}$ as a reasonable regulatory value for average fish consumption, it is clear that most fish analyzed are below this limit. Thus regulation of STB may not be required at the same level for these fish as has been promulgated for MD reservoir fish.

2.   Concentrations of MeHg in LMB caught in the tidal tributaries of the Chesapeake Bay have lower concentrations than LMB residing in reservoirs, for fish of similar size. Thus, this confirms the notion that estuarine fish accumulate less MeHg than fish in reservoirs or lakes, likely primarily as a result of lower MeHg levels in estuarine waters. While levels of MeHg are lower in LMB from the tidal tributaries, the concentrations do increase with age such that the larger fish (>2 kg) will have levels greater than 300 ng g$^{-1}$.

3.   For WHP, levels of MeHg were low, especially for fish from the upper reaches of the Bay. For most fish analyzed, MeHg concentrations were <100 ng g$^{-1}$.

4.   Otolith analysis showed that STB from the mainstem Chesapeake Bay came from both resident and migratory populations. There was, however, insufficient statistical

difference in MeHg concentration between these subpopulations that confounded factors in interpretation, and limited the conclusions about the role of migration in influencing MeHg levels in STB from the Chesapeake Bay.

       5. The estuarine fish (STB and WHP) appeared to have a lower % MeHg in their tissues that would have been predicted based on previous results. Other recent studies have found similar trends. The reason for this requires further investigation.

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## APPENDIX I: LENGTH, WEIGHT and METHYLMERCURY CONCENTRATION IN FISH.

**Fish collected in Fall 2002**

| Fish ID | Location | Length (inches) | Weight (g) | MeHg (ng/g) |
|---|---|---|---|---|
| *Largemouth Bass* – **Upper Bay (3 locations)** | | | | |
| LB1 | SUS100802 | 15.25 | 525 | 3.30 |
| LB2 | SUS100802 | 15.25 | 510 | 13.02 |
| LB3 | SUS100802 | 15.5 | 550 | 8.54 |
| LB4 | SUS100802 | 16 | 570 | 9.99 |
| LB5 | SUS100802 | 16.25 | 610 | 15.34 |
| LB5 | SUS100802 | 16.5 | 640 | 14.97 |
| LB6 | SUS100802 | 17 | 685 | 5.48 |
| LB6 | SUS100802 | 17.25 | 735 | 8.96 |
| LB1 | SWS100802 | 15.5 | 540 | 15.61 |
| LB2 | SWS100802 | 15.5 | 525 | 16.81 |
| LB3 | SWS100802 | 17.5 | 760 | 28.50 |
| LB4 | SWS100802 | 18 | 800 | 27.91 |
| LB5 | SWS100802 | 16 | 590 | 17.25 |
| LB5 DUP | SWS100802 | 16 | 590 | 11.90 |
| SB1 | SWS100802 | 16.5 | 640 | 11.73 |
| LB1 | UBY101502 | 15.5 | 530 | 9.39 |
| LB1 DUP | UBY101502 | 15.50 | 530 | 11.90 |
| LB2 | UBY101502 | 16.50 | 652 | 7.67 |
| LB3 | UBY101502 | 17.25 | 708 | 20.24 |
| LB4 | UBY101502 | 17.50 | 750 | 20.81 |

| *Striped Bass* – **(Deale (2 locations)** | | | | |
|---|---|---|---|---|
| SB1 | DEA091602 | 19 | 994 | 16.22 |
| SB2 | DEA091602 | 19.75 | 1036 | 14.27 |
| SB3 | DEA091602 | 17.75 | 829 | 10.86 |
| SB3 DUP | DEA091602 | 17.75 | 829 | 11.36 |
| SB4 | DEA091602 | 18 | 1071 | 9.76 |
| SB5 | DEA091602 | 19.75 | 817 | 10.41 |
| SB6 | DEA091602 | 21 | 1492 | 12.92 |
| SB7 | DEA091602 | 21 | 1115 | 41.44 |
| SB8 | DEA091602 | 21 | 1388 | 26.11 |
| SB9 | DEA091602 | 20.5 | 1134 | 64.05 |
| SB10 | DEA091602 | 20.5 | 1193 | 19.22 |
| SB11 | DEA091602 | 24 | 1775 | 236.10 |
| SB12 | DEA091602 | 24 | 1783 | 91.26 |
| SB13 | DEA091602 | 22.25 | 1405 | 92.58 |
| SB14 | DEA091602 | 25 | 2147 | 26.36 |
| SB15 | DEA091602 | 22 | 1602 | 13.19 |
| SB1 | DEA092402 | 19 | 1025 | 26.49 |
| SB2 | DEA092402 | 18.5 | 1040 | 43.56 |
| SB3 | DEA092402 | 17.75 | 992 | 16.14 |
| SB4 | DEA092402 | 19.75 | 1004 | 206.54 |
| SB5 | DEA092402 | 18.5 | 957 | 21.29 |
| SB6 | DEA092402 | 19.75 | 1072 | 59.48 |
| SB7 | DEA092402 | 20.5 | 1053 | 76.99 |
| SB8 | DEA092402 | 21 | 1267 | 36.46 |
| SB9 | DEA092402 | 20.75 | 1225 | 43.18 |
| SB10 | DEA092402 | 20.25 | 987 | 210.20 |
| SB10 DUP | DEA092402 | 20.25 | 987 | 188.15 |
| SB11 | DEA092402 | 21.5 | 1228 | 207.80 |
| SB12 | DEA092402 | 21.5 | 1414 | 219.69 |
| SB13 | DEA092402 | 22.25 | 1618 | 171.36 |
| SB14 | DEA092402 | 22.25 | 1276 | 168.30 |
| SB15 | DEA092402 | 21.75 | 1436 | 163.53 |

| Striped Bass - **Point Lookout** | | | | |
|---|---|---|---|---|
| SB1 | PTL091702 | 19.25 | 909 | 26.80 |
| SB2 | PTL091702 | 20 | 1251 | 30.92 |
| SB3 | PTL091702 | 18.5 | 781 | 23.43 |
| 3 DUP | PTL091702 | 18.5 | 781 | 20.65 |
| SB4 | PTL091702 | 19.25 | 735 | 88.08 |
| SB5 | PTL091702 | 17.5 | 518 | 25.67 |
| SB6 | PTL091702 | 21.5 | 1210 | 55.27 |
| SB7 | PTL091702 | 22 | 1410 | 40.80 |
| SB8 | PTL091702 | 20.5 | 1064 | 50.74 |
| SB9 | PTL091702 | 21.25 | 1923 | 11.72 |
| SB10 | PTL091702 | 20.5 | 1350 | 122.31 |
| SB11 | PTL091702 | 22.75 | 1339 | 66.41 |
| SB12 | PTL091702 | 23.75 | 1803 | 55.76 |
| SB14 | PTL091702 | 25.25 | 2443 | 54.58 |
| SB15 | PTL091702 | 25.25 | 1339 | 47.81 |

# Fish Collected in Spring 2003

| Sample ID | Length (inches) | Weight (g) | MeHg (ng/g) |
|---|---|---|---|
| *Striped Bass* | | | |
| ANS03-1 | 36 | 7710 | 102.94 |
| ANS03-2 | 32 | 5215 | 76.35 |
| ANS03-3 | 39 | 9297 | 126.23 |
| ANS03-4 | 38 | 9524 | 251.01 |
| ANS03-5 | 37 | 8390 | 111.12 |
| ANS03-6 | 35 | 6485 | 39.52 |
| ANS03-7 | 37 | 7800 | 215.31 |
| ANS03-8 | 36.5 | 7166 | 152.16 |
| ANS03-9 | 46.5 | 17234 | 349.37 |
| ANS03-10 | 36 | 6349 | 138.52 |
| ANS03-11 | 38 | 8163 | 187.00 |
| ANS03-11 dup | 38 | 8163 | 227.00 |
| ANS03-12 | 36 | 6803 | 216.66 |
| ANS03-13 | 36 | 6803 | 220.24 |
| ANS03-14 | 38 | 7710 | 136.64 |
| ANS03-15 | 38 | 9524 | 236.97 |
| ANS03-16 | 38 | 9070 | 277.00 |
| ANS03-17 | 30.5 | 4626 | 18.49 |
| ANS03-18 | 33.5 | 7664 | 136.67 |
| ANS03-19 | 38 | 8798 | 147.63 |
| ANS03-19 dup | 38 | 8798 | 140.19 |
| ANS03-20 | 29 | 3356 | 65.76 |
| ANS03-21 | 42 | 14739 | 126.90 |

| Sample ID | Length (mm) | Weight (g) | MeHg (ng/g) |
|---|---|---|---|
| White Perch – **Severn R** | | | |
| SEV040203 WP1 | 183 | 87.58 | 1.89 |
| SEV040203 WP2 | 174 | 67.49 | |
| SEV040203 WP3 | 172 | 71.54 | 6.82 |
| SEV040203 WP4 | 189 | 88.84 | 6.96 |
| SEV040203 WP5 | 189 | 93.89 | 2.61 |
| SEV040203 WP6 | 202 | 118.11 | 7.13 |
| SEV040203 WP7 | 192 | 96.55 | 4.18 |
| SEV040203 WP8 | 206 | 116.77 | 2.40 |
| SEV040203 WP9 | 207 | 118.14 | 13.73 |
| SEV040203 WP10 | 211 | 125.14 | 3.24 |
| SEV040203 WP10 dup | 211 | 125.14 | 3.81 |
| SEV040203 WP11 | 224 | 172.5 | 11.25 |
| SEV040203 WP12 | 239 | 194.36 | 15.87 |
| SEV040203 WP13 | 218 | 162.5 | 15.96 |
| SEV040203 WP14 | 217 | 152.39 | 6.18 |
| SEV040203 WP15 | 207 | 163.44 | 9.72 |
| *White Perch* - **Choptank R** | | | |
| Chp 040203 WP2 | 173 | 91.79 | 0.54 |
| Chp 040203 WP3 | 178 | 76.38 | 4.65 |
| Chp 040203 WP4 | 178 | 73.87 | 2.95 |
| Chp 040203 WP5 | 189 | 91.54 | 26.30 |
| Chp 040203 WP6 | 200 | 97.42 | 35.19 |
| Chp 040203 WP7 | 203 | 105.87 | 13.78 |
| Chp 040203 WP7 dup | 203 | 105.87 | 15.60 |
| Chp 040203 WP8 | 199 | 102.2 | 41.51 |
| Chp 040203 WP9 | 193 | 85.76 | 7.78 |
| Chp 040203 WP10 | 208 | 117.58 | 22.64 |
| Chp 040203 WP11 | 248 | 211.72 | 30.55 |
| Chp 040203 WP12 | 211 | 127.01 | 14.05 |
| Chp 040203 WP14 | 245 | 220.66 | 7.07 |
| Chp 040203 WP15 | 237 | 209.59 | 29.09 |